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ORGANO-METALLIC AND ORGANO-METALLOIDAL HIGH-TEMPERATURE LUBRICANTS AND RELATED MATERIALS

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TECHNICAL REPORT AFML–TR–64–383, Pt. II

FEBRUARY 1966

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright–Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by Iowa State University of Science and Technology, Ames, Iowa, under USAF Contract No. AF 33(615)-2368. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division with Dr. Christ Tamborski and George J. Moore acting as project engineers.

This report covers work conducted from 15 December 1964 to 15 December 1965. The authors are: Henry Gilman, Dwain Chapman, Peter J. Morris, Robert L. Harrell, See-Yuen Sim and Clifford L. Smith.

Acknowledgement. The authors are grateful to Mr. A. W. Schlueter for the X-ray powder photographs and to Mrs. Akiko Irie for the infrared spectra. We also wish to thank Dr. J. M. Holmes for his assistance with this report.

Manuscript released by authors December 1965 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

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ABSTRACT

This report describes some entirely novel types of organosilicon compounds. They are primarily polyfunctional monomers. The functional groups may be alike or unlike, and the symmetry with some is unique in being of the highest possible order. These polyfunctional organosilicon monomers should provide avenues to the preparation of polymers with diverse and promising properties. Among the polyfunctional types are such highly reactive species as $(HMe_2Si)_4Si$ and $(HMe_2Si)_3SiLi$.

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I. INTRODUCTION

Embodied in this report is an account of the extension of our studies concerned with the preparation of reactive organosilicon monomers for use in the synthesis of organosilicon polymers.

Some of these monomers contain highly unusual structures. Among such are grouping which are not only entirely symmetrical such as $(Me_3Si)_4Si$, but also highly symmetrical types having polyfunctional units such as $(HSiMe_2)_4Si$. The liquid state of many of these compounds posed a special problem in some aspects of separation and identification, insofar as boiling points are concerned, as supplements to other conventional procedures such as gas phase chromatography. For this reason we have examined a broadly useful tool: namely, boiling point numbers by relatively simple calculations for use in obtaining the boiling points of these polysilanes for comparison purposes.

One of the entirely novel types is the simple permethylated completely symmetrical organosilicon compound: namely, tetrakis(trimethylsilyl)silane, which is conveniently prepared as follows:

$$Me_3SiCl + SiCl_4 + Li \longrightarrow (Me_3Si)_4Si$$

This compound is characterized by high melting point, ease of sublimation, and more than average thermal stability. A related type is tetrakis(dimethylsilyl)silane, $(HMe_2Si)_4Si$. This was prepared by a perfectly analogous simple reaction starting with the available HMe_2SiCl. Not only does this highly symmetrical organosilicon compound have some promising special physical characteristics, but it has four functional Si-H groups. These highly reactive linkages should provide an avenue of approach to new polymers. Various routes can be taken from the monomers to the polymers but one which may be particularly attractive is that which involves addition of Si-H to carbon-carbon double and triple bonded unsaturated systems. These should provide new types of polymers having varying degrees of symmetry. No such synthetic approaches are currently available in organosilicon chemistry. Furthermore, it is probable that the types of reactions need not be restricted to simple organosilicon compounds, but may involve appropriately substituted types where the silicon may be replaced by a variety of metals and metalloids and where substituent atoms and groups may include particularly such elements as fluorine.

Another most promising type has been developed. This comprises two of the highly reactive groupings, but contained in one molecule, namely, an Si-Li functional group and an Si-H moiety, prepared as follows:

$$(HMe_2Si)_4Si + MeLi \longrightarrow (HMe_2Si)_3SiLi$$

These unique organosilyllithium compounds, found to be very conveniently prepared and of a high order of synthetic versatility, were unexpected partly because it has hitherto been postulated that availability of such types required the presence of one or more aryl groups. Some preliminary chemical and physical properties of the $(HMe_2Si)_3SiLi$, and related types, are described in this report.

There is another aspect of our studies on the synthesis of polyfunctional monomers, which are potential starting materials for polymers having interesting and useful characteristics. Among these polyfunctional monomers are those which not only are polysilanes but also have aryl groups such as phenyl and siloxane units. A precursory compound is the commercially available diphenyldichlorosilane. From this one can obtain in excellent yield the 1,4-dichlorooctaphenyltetrasilane, $Cl(Ph_2Si)_4Cl$. This alpha, omega-dichloro compound is readily converted to octaphenyloxatetrasilacyclopentane (see the relevant Discussion section of this report for structural formulas and reaction sequences). Such siloxanes have interesting properties which are associated with the siloxane units, the aryl groups, and the polysilane heterocycles of different sizes. Among other types, one can prepare from them cyclic polysiloxanes of larger sizes, and (by chlorine cleavage) readily available, synthetically useful higher linear alpha, omega-dichloro derivatives. The sequence of reactions developed provides a ready conversion of the polyfunctional monomers to new types of polymers.

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II. AN ATTEMPTED CORRELATION OF THE BOILING POINTS OF ORGANICALLY SUBSTITUTED POLYSILANES

In correlating the boiling points of hydrocarbons C. R. Kinney[1] developed the empirical relationship boiling point (b.p. °C) = $230.14 \sqrt[3]{B.P.N.} - 543$ where the boiling point number (B.P.N.) is "the sum of the individual atomic and group boiling numbers expressing the structure of the molecule". Using this basic relationship between boiling point (b.p.) and B.P.N., R. N. Lewis and A. E. Newkirk[2] in 1947 extended the application of the above relationship to polysubstituted monosilanes. Whereas Kinney used atomic B.P.N. values which he derived from the normal paraffin hydrocarbons, Lewis and Newkirk found it more convenient to think mainly in terms of hydrocarbon group B.P.N. values. The B.P.N. of a polysubstituted silane is in general an additive function of the group B.P.N.'s the value of which varied according to the degree of substitution. Thus according to Lewis and Newkirk's paper, "the B.P.N. of a methyl group decreases in the series $MeSiH_3$ (3.43), Me_2SiH_2 (3.17), Me_3SiH (3.02), and Me_4Si (2.74)...". The hydrocarbon group substituent in the silane has a unique value depending on the total number of organic groups present. Thus in the case of mixed alkyl silanes the B.P.N. of each alkyl group depends on the total number of alkyl groups in the molecule. For instance the B.P.N.'s of methyl and ethyl groups in dimethyldiethyl-silane are the same as in tetramethylsilane (2.74) and tetraethylsilane (5.89). The only atomic B.P.N. values used by Lewis and Newkirk (L. and N.) are those of Si, H, and halogen. The first two were given values of Si, 4.20 and H, 0.60 derived from the polysilanes Si_nH_{2n+2}. Fig. I shows the linear relationship between the B.P.N. of the polysilane and the number of silicon atoms. This means that the increase in chain length by the silylene unit, $-SiH_2-$, always increases the boiling point by the same increment, i.e. 5.3. This illustrates that a given group makes the same contribution to the B.P.N. of any compound in which its environment is identical. Thus the data for the polysilanes indicates that the general formula for the B.P.N. of any polysilane $H(SiH_2)_nH$ is equal to 1.5+n.(5.3), where n $\geqslant$ 2. Thus for the polysilanes 2x(B.P.N. for H) equals 1.5 and B.P.N. Si + 2x(B.P.N. for H) = 5.32; i.e. B.P.N. for H is 0.75 and for Si, 3.82. This is in contrast with L. and N.'s values of 0.60 and 4.20, respectively, for a monosilane, which according to Fig. I do not quite fit the overall pattern. The following, Table I, compares the newly derived data with that of L. and N. It will be noticed that the greatest discrepancy

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is for the monosilane. Naturally as L. and N.'s data is

Table I

$H(SiH_2)_n H$	b.p. °C	Ref.	Observed B.P.N.	L. and N. B.P.N.	New B.P.N.
n					
1	-111.9	2(a)	6.57	6.6	6.82
2	- 14.5	2(a)	12.12	12.0	12.14
3	52.9	2(a)	17.38	17.4	17.46
4	109	2(a)	22.75	22.8	22.78

for application to monosilanes, they weighted more heavily
the observed monosilane boiling point, and their calcu-
lations were more suited to this compound than to the
higher members of the series. However, when the latter
are of prominent interest then the newly derived values
are desirable. Before proceeding to discuss the organi-
cally substituted polysilanes it is of interest to briefly
investigate the change in B.P.N. of a monosilane as the
carbon chain length of one or two of the hydrocarbon groups
is increased. This feature will be best understood by
considering the series $C_n H_{2+n}-\overset{H}{\underset{H}{Si}}-C_n H_{2+n}$, for which there
is comprehensive data. It is interesting in this connection
to note that L. and N. remarked almost in conclusion, that
silicon compounds containing more complex groups than those
discussed in their paper (which dealt only with Me, Et,
nPr, and Ph groups) could probably be calculated by using
also Kinney's data. They quote the example of a B.P.N. of
nBu·Me$_3$Si which could be derived by addition of 2.8, the
value for -CH$_2$-, to that B.P.N. calculated for nPrMe$_3$Si.
Thus the calculated b.p. of 112.2° compares well with that
of the observed value of 115.4°C. Table II shows the
b.p.'s and calculated B.P.N.'s for the $(C_n H_{2+n})_2 SiH_2$ series
and Fig. I shows the B.P.N. to be a linear function of the
number of carbon atoms. The gradient of 2.8 is the actual

Table II

$(C_n H_{2+n})_2 SiH_2$	n	Ref.	Observed b.p. °C	Observed B.P.N.
Me$_2$SiH$_2$	2	3,4	- 19.6	11.74
Et$_2$SiH$_2$	4	4,5	56	17.64
nPr$_2$SiH$_2$	6	5,6,7	111	22.97
nBu$_2$SiH$_2$	8	7	160	28.69

FIG. I

SCALE FOR
⊙ $(C_nH_{2+n})_2SiH_2$
AND ⊗ $H(SiH_2)_nH$

SCALE FOR
⊙ $H(SiMe_2)_nCl$
AND ⊡ $H(SiMe_2)_nH$

B.P.N.

B.P.N.

n

ta

28 24 20 16 12 8 4 0

48 40 32 24 16 8

0 1 2 3 4 5 6 7 8
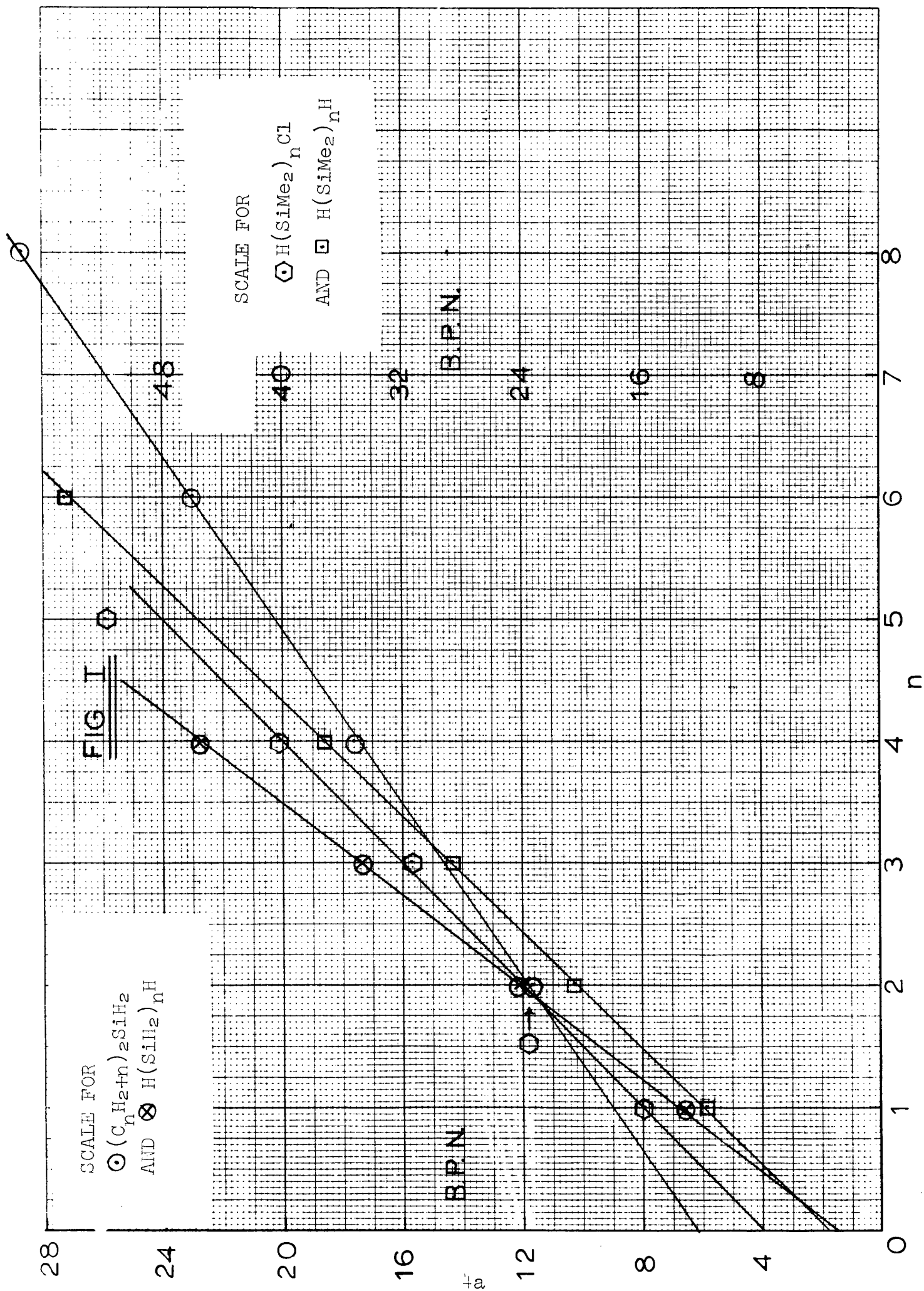
B.P.N. increase due to a $-CH_2-$ group, and has exactly the same value as predicted and mentioned earlier. What is also of interest is that the ordinate intercept of 6.3 gives the B.P.N. of the silylene[8] portion of the molecule. Thus in the dialkyl silanes the $-SiH_2-$ silylene group has a B.P.N. of 6.3 whereas in the polysilanes it has the value of 5.32. This illustrates that not only does the amount of substitution of the parent silane affect the B.P.N. value of the substituent group but also alters the atomic B.P.N.'s of the silicon and hydrogen atoms, a feature which was not easy to predict and not recognized by L. and N.

Fortunately all the data up to this stage has been for materials of sufficiently low molecular weight to give boiling points measurable at 760 mm. Just prior to proceeding to discussion of organopolysilanes it is pertinent to mention the procedure used for converting boiling points at reduced pressure to the corresponding boiling point at a standard atmosphere (760 mm.). For this purpose a Vapor-Pressure-Temperature Nomograph[9] was used. For an accurate conversion it is necessary to know the boiling point at different pressures or the vapor pressure at different temperatures, and as in most cases of reported boiling points there is only the one value, the converted boiling point therefore is no more than an approximation. The accuracy is even less for boiling points at low pressures as measurement of the latter values requires a particularly careful experimental technique. In some cases, particularly for the $Ph(SiMe_2)_nPh$ series, there are conflicting boiling point values, and it has been found expedient to weight more heavily those values determined at the highest pressure. As will be seen later a combination of these two factors could well explain discrepancies just as logically as a more sophisticated physicochemical argument.

Table III shows the data for the permethylated polysilanes, which is the most studied homologous series relevant to this discussion. Although L. and N. specifically state that their values are not suitable for disilanes it is of interest to note the increasing discrepancy between the calculated and observed B.P.N.'s with the increasing chain length. Fig. II, plot 1, shows the pseudo linear relationship of the overall situation where the B.P.N. of $Me(SiMe_2)_nMe$ equals $9.0+n$ (7.01). However, according to

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Table III

Me(SiMe$_2$)$_n$Me n	b.p. °C/mm.	Ref.	b.p. °C 760 mm.	Observed B.P.N.	L. and N. B.P.N.
1	26.6/760	3,4	266	15.16	
2	113/760	10	113	23.06	26.52
3	175-176/760	11,12	175-176	30.38	36.88
4	109/15	11,12	233	38.37	47.24
5	133-136/13	12	269	43.96	57.60
6	165/10	12	309	50.23	67.96
7	194/1.6	12	335	55.56	78.32
8	194-198/3	13	385	64.96	88.68
9					
10	244/3	13	445	79.20	99.04

plot 2, the B.P.N. of Me(SiMe$_2$)$_n$Me equals 7.5+n (7.70) where 4 > n > 1, and plot 3 shows the B.P.N. of Me(SiMe$_2$)$_n$Me equals 15.5+n (5.8) where 7 > n > 4. It is perhaps a coincidence as a result of slight discrepancies in experimental values that the different plots can be made, and it would have been more reasonable to place the first seven points on a curve had it not been for the two higher homologues. However, in order to make comparisons with the other homologous series the linear relationship between the lowest members of the permethylated homologous series is of interest. Up to n is 4 the terminal Me groups have a B.P.N. of 3.75 each, and successive dimethylsilylene groups, -SiMe$_2$-, contribute 7.7 to the B.P.N. This is equivalent to a B.P.N. for Si of 3.82, and 1.59 each for the Me groups. The lowest B.P.N. value of a Me group reported by L. and N. was 2.74 in a tetra-substituted organosilane. They also noted that, "the diminution of the B.P.N. of an organic group with increasing substitution is probably a bulk effect. The greater diminution in the B.P.N. of halogens, especially in view of their small size, is probably due mainly to some other cause, possibly the action of polarity or resonance[14]". It is

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pertinent to mention at this stage that the application of
the Kinney equation and the true additive nature of group
B.P.N.'s only holds if there is no molecular association.
For the permethylated series this factor should be at a
minimum and be definitely less than in any other series
studied. However, the best linear relationship is shown
by the $H(SiMe_2)_nH$ series over the whole range of the avail-
able data. This would suggest that association factors
are absent or constant for this series. However, as the
chain length would almost certainly affect the actual
amount of association, the extent of the association if
present would very likely differ along the series, giving
a non-linear relationship between n and B.P.N. It would
therefore seem that association for the $H(SiMe_2)_nH$ series
is absent. This contrasts observations[18] made during
measurements of molecular weight (osmometrically in ben-
zene and acetone[15]) on polysilanes containing Si-H and
Si-Me groups particularly in branched chain compounds,
where anomalously high molecular weight values could be
attributed to association factors. Over the range $1 \leqslant n \leqslant 4$
all series later shown have fair linearity, indicating
the validity of the concept that silyl and silylene group
B.P.N. values are additive.

Tables IV-VII give the data for the other homologous
series, which are plotted on Figs. I and II.

Table IV

$Cl(SiMe_2)_nCl$

n	Observed b.p. °C/mm.	Ref.	b.p. °C/760 mm.	Observed B.P.N.
1	70.5/760	16	70.5	18.92
2	148/760	17	148	27.08
3	82-83/11[a]	17	203	34.07
4	76-78/1.0[b]	19	248	40.64
5	-----			
6	143-144/.02[c]	18	420	73.30

B.P.N. values - Cl end group, 7.5 each; -SiMe₂- dimethyl-
silylene unit, 6.48.
(a) Independent studies[19] give a confirmatory b.p. 89-92°C/
15 mm.; (b) Kumada et al recently published the b.p. as
98°C/15 mm. i.e. 242°C/760 mm.; (c) Independent studies[19]
give the b.p. 160-162°C/0.8 mm. Material subsequently
isolated[18] with this physical constant has been shown by
vapor phase chromatography to contain some dodecamethyl-
cyclohexasilane.

Table V

$H(SiMe_2)_nH$

n	Observed b.p. °C/mm.	Ref.	b.p. °C/760 mm.	Observed B.P.N.
1	-19.6/760	3,4	-19.6	11.74
2	88/760	20	88	20.62
3	54/22	21,18	161	28.65
4	-----	22	225[a]	37.19
5	-----			
6	103/.12	18	330	54.62

B.P.N. values - H end group, 1.8 each; -SiMe₂- dimethyl-silylene unit, 8.40.

(a) Kumada et al[21] report, in our opinion erroneously, that the b.p. is 74°/19 mm., i.e. 185°/760 mm.

Table VI

$H(SiMe_2)_nCl$

n	Observed b.p. °C/mm.	Ref.	b.p. °C/760 mm.	Observed B.P.N.
1	34.7-36/760	23	34.7-36.0	15.85
2	119-120/760	24	119-120	23.82
3	76/18	24	183	31.41
4	58-59/0.4	24	243-247	40.17
5	80-82/.05	24	315[a]	51.8
6	-----	24	⤹360[a]	60.45

(a) Preliminary values only; to be confirmed.
B.P.N.'s; end groups H+Cl, 8.0; -SiMe₂-, 8.04.

FIG Ⅱ

Table VII

$Ph(SiMe_2)_n Ph$
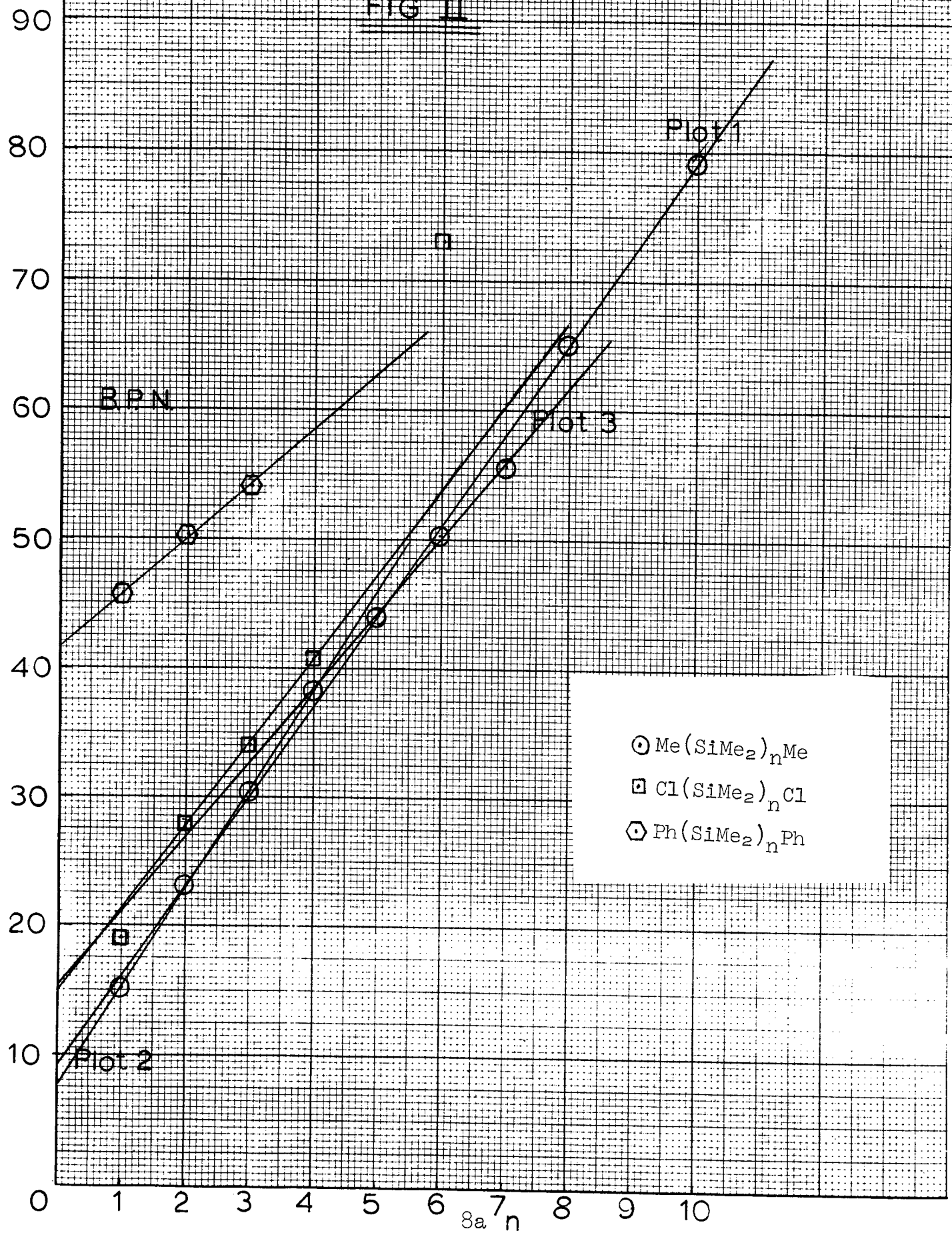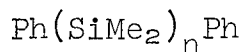
n	Observed b.p. °C/mm.	Ref.	b.p. °C/760 mm.	Observed B.P.N.
1	176-180/45[a]	25	280	45.76
2	128-130/1.8[b]	26	306	50.23
3	122/.4-.45[c]	24	327	54.05
4	no b.p. recorded			

B.P.N.'s - Ph end groups, 20.8 each; -SiMe₂- group 4.23.

(a) H. C. Kaufmann in his book[25] gives b.p.'s:- 275.5-276.5°/760 mm.; 176-8°/45 mm.; and 89/0.2 mm. The first value is a high temperature at which to measure a boiling point, and the second value was the most acceptable since the pressure was not low enough to raise doubts as to its accuracy. (b) Other boiling points are 110°/0.25 mm.[27], and 73°/.01 mm.[28] (c) An alternative value is 120-122°/0.15 mm.[27]

Table VIII shows the B.P.N. values of the end groups and dimethylsilylene groups for the different series. The varying B.P.N. values of the dimethylsilylene group illus-

Table VIII

$X(SiMe_2)_n Y$
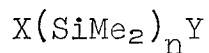
	Observed end-group B.P.N.	B.P.N. of -SiMe₂- group
X=Y=Me	Me, 3.75	7.00 (7.70, $1 \leqslant n \leqslant 4$)
X=Y=H	H, 1.8	8.40
X=H, Y=Cl	H+Cl, 8.0	8.04
X=Y=Cl	Cl, 7.5	6.48
X=Y=Ph	Ph, 20.3	4.23

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trates that there is no apparent way of predicting its
value unless the nature of the end group(s) is known.
The apparent B.P.N. values of the hydrocarbon and atomic
end groups as indicated in Table VIII have little meaning.
In fact, in dealing with any polysilane it is best to think
in terms of substituted silyl groups as end groups of the
type XMe_2Si-. The assignment of a B.P.N. to a group con-
taining silicon is a new concept. L. and N. by using
hydrocarbon group B.P.N.'s could obtain good results for
straight and highly branched hydrocarbon compounds whereas
the previous studies by Kinney had involved atomic B.P.N.'s.
Similarly it is intended here to demonstrate and develop
the usefulness of the concept of organosilyl group B.P.N.'s
in predicting the boiling point of polysilanes including
those with branched chains. In order to do this the follow-
ing basic silyl group assignments (Table IX) have been
derived from the organodisilanes. Table X compares the
calculated and observed values for most of the disilanes
on which to date there is information. In general there
is good agreement between values, the notable exception
being for the higher boiling materials e.g., $Me_2PhSi \cdot SiPh_2Me$

Table IX

Silyl group B.P.N. assignments

H_3Si	6.06	Cl_3Si	15.57
H_2MeSi	8.51	Cl_2MeSi	14.26
HMe_2Si	10.31	$ClMe_2Si$	13.00
Me_3Si	11.53	F_3Si	8.50[b]
		F_2MeSi	9.51[b]
Ph_3Si	51.96	FMe_2Si	10.52
Ph_2MeSi	39.40	$BrMe_2Si$	15.50
$PhMe_2Si$	25.12	IMe_2Si	-----
$PhMeHSi$	24.01[b] (28.00[a])		
$PhEtHSi$	28.45	Et_3Si	20.63
$PhEt_2Si$	31.00	Et_2MeSi	17.52
		$EtMe_2Si$	14.85
$EtO \cdot Me_2Si$	14.90	$EtMeHSi$	12.87
$(EtO)_2MeSi$	17.55		
$(EtO)_3Si$	21.05		

(a) observed value, (b) calculated value, see text.

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Table X

Disilanes

	b.p. °C/mm.	Ref.	b.p. °C/760	Observed B.P.N.	Calculated B.P.N.	b.p. °C/760 mm.[a]
(H₃Si)₂	-14.5/760	2a	-14.5	12.12	---	---
(HMe₂Si)₂	88/760	20	88	20.62	---	---
(Me₃Si)₂	113/760	10	113	23.06	---	---
Me₃Si·SiMe₂H	97.5/715	29,30	100	21.82	21.84	100.5
H₂MeSi·SiMe₂H	68-9/760	21	69	18.82	18.82	69
(H₂MeSi)₂	49/760	21	49	17.03	---	---
Me₃Si·SiMe₂Cl	134-135.6/760	11	135	25.58	23.44	117
HMe₂Si·SiMe₂Cl	119-120/760	24	120	23.82	23.31	117
Cl₂MeSi·SiMe₂Cl	155/760	25	155	27.80	---	---
(ClMe₂Si)₂	148/760	17	148	27.05	26.00	139.5
Me₃Si·SiCl₃	146-152/760	31	149	27.10	---	---
Cl₂MeSi·SiCl₃	51-52.5/10	32	176	29.70	29.83	170.5
(Cl₃Si)₂	90/125	33	150	27.2	31.14	181
ClMe₂Si·SiMe₂F	120/760	34,17	120	23.80	24.06	123
ClH₂Si·SiH₂Cl	----	35	---	---	18.80	70.5
H₃Si·SiH₂Cl	----	35	---	---	15.46	30
(PhMe₂Si)₂	128-130/1.8	26	306	50.23	---	---
HMe₂Si·SiMe₂Ph	111.5-112/27	27	215	35.76	35.43	213
Me₃Si·SiMe₂Ph	95-95.5/11	27,36,37	220	36.45	36.65	221.5
Me₃Si·SiMePh₂	98-99/0.23	27,36	310	50.93	---	---
HMePhSi·SiMe₂Ph	86-87/.05	38	322	53.13	49.13	300
(HMePhSi)₂	81-83/.003	39	≤450	80.4	48.02	294

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Compound						
Me₃Si·SiPh₃	218-220/11	39,37,40	375	63.49	—	—
Me₂PhSi·SiPh₂Me	156-157/.17	27	401	69.07	64.52	374
PhMe₂Si·SiMe₂Cl	119/20	21	235	38.67	37.03	224
ClPh₂Si·SiMe₂Ph	157/.005	41	457	82.00	55.95	337
HPh₂Si·SiMe₂Ph	126-7/.002	41	415	72.20	61.78	367
(FMe₂Si)₂	92-93/760	17,42,43	93	21.05	—	—
FMe₂Si·SiMe₃	103/760	17,42,43, 44	103	22.0	22.05	102.5
(BrMe₂Si)₂	79-82/30	12,20	180	31.00	—	—

Silanes Containing Ethyl Groups

Compound						
(Et₃Si)₂	252/760	45,46	252	41.26	—	—
(EtMe₂Si)₂	168-170/760	38	170	29.7	—	—
(Et₂MeSi)₂	207-212/760	47	210	35.04	—	—
HEt₂Si·SiEt₃	78-83/1.5	48	250	40.95	—	—
MeEt₂Si·SiMe₂Et	192-194/760	47	194	32.80	36.41	220
Me₂EtSi·SiMeEt₂	125/40	55	221	37.6	32.37	191
Me₃Si·SiEt₃	192-194/760	50	193	32.70	—	—
Me₃Si·SiMeEt₂	168-171/760	49	170	29.76	32.16	190.5
Me₂EtSi·SiEt₃	207-12/760	51	210	35.0	29.05	165
Et₃Si·SiEt₂Ph	144/3.5	52	300	49.17	35.48	219
(HEtPhSi)₂	110-111/0.1	53,39	342	56.89	—	—
(PhEt₂Si)₂	190-192/3.5	52	372	62.88	—	—
Et₃Si·SiHEtMe	140/140	54	199	33.5	—	—
BrEt₂Si·SiEt₃	88/2	56	250	40.95	—	—

Disilanes Containing Ethoxy Groups

Compound	b.p.					
EtO·Me₂Si·SiMe·(OEt)₂	85.5-87/21	17	196	33.1	32.45	191
(EtO)₂·MeSi·SiMe·(OEt)₂	101.5-102/22	17,12	211	35.1	35.74	215
Me₃Si·SiMe₂·OEt	143.5-144.5/760	17	145	26.7	26.43	142.5
(EtO·Me₂Si)₂	169-170/760	17	170	29.75	----	----
(EtO)₂MeSi·SiMe₂·OEt	72.5-74/13	57	194	32.80	32.72	190
Et₃Si·Si(OEt)₃	123/15	59	250	41.05	41.68	255
(EtO)₆Si₂	145/25	59	257	42.10	----	----
EtO·Me₂Si·SiMe₂Ph	121/20	21	236	38.8	40.02	243.5

(a) Where the calculated b.p. °C, and B.P.N. are not quoted the observed b.p. has been used to derive the silyl group B.P.N. value.

and other more fully polyphenylated compounds. However, the observed boiling points for these compounds are all at low and very low pressures and it has been mentioned earlier that this raises doubts about their validity. Values for silyl groups containing ethyl groups are included although the restricted amount of data in this region permits only preliminary assignments.

It has been found possible to make some correlation between related silyl groups of the type $X_nY_{3-n}Si$ and assess the individual validities. If we consider the series $Me_nH_{3-n}Si$ for which there is complete data we find it is possible to plot for each, the B.P.N. as ordinate against the number of carbon atoms as abscissa (see Fig. III). Although this particular series falls on a slight curve whose gradient is approximately 1.72, linear relationships are found to exist for the $Me_nEt_{3-n}Si$, $Me_nCl_{3-n}Si$, and $Me_nPh_{3-n}Si$ series where the gradients are, respectively, 3.04, 1.38 and 13.70. The figures represent the increase in B.P.N. of the silyl group by replacing one of the substituents by an atom or group with a greater B.P.N. What is more important is that successive replacements cause the same increase in B.P.N. Making this important assumption the B.P.N. values of the following silyl groups with mixed substituents are predicted, by interpolation, and listed in Table XI. Table X includes the b.p. °C using the above data for the compounds

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Table XI

Predicted B.P.N. values for silyl groups with mixed substituents

H_2EtSi	10.92	HPh_2Si	36.66
HEt_2Si	15.78 (20.32^{a})	H_2PhSi	21.36
	Δ Et-H 4.86		Δ Ph-H 15.30
H_2ClSi	9.40	Ph_2EtSi	41.51
HCl_2Si	12.50	$PhEt_2Si$	31.07 (31.44^{a})
	Δ Cl-H 3.34		Δ Ph-Et 10.44
Ph_2ClSi	30.83		
$PhCl_2Si$	27.70		
	Δ Ph-Cl 12.13		

(a) observed value.

$(H_2ClSi)_2$ and $H_3Si \cdot SiH_2Cl$ which have been reported without physical properties. It will be noticed that a few assignments have been made contrary to some individual observed values. Notably $(Cl_3Si)_2$ gives a B.P.N. for $-SiCl_3$ of 13.6 whereas a value of 15.57 fits the general pattern. It is very likely that the fully halogenated disilane has an anomalous boiling point in association of molecules resulting from the ionic character of the Si-Cl bond. Also all observed data with respect to the $-SiMePhH$ group is suspect, and the suggested value (Table X) was derived from that of the $-SiMe_2H$ group. Thus the suggested value of 24.01 is the sum of 10.31 (B.P.N. of $-SiMe_2H$) and 13.7 (Δ Ph-Me i.e. the gradient of the $Ph_nMe_{3-n}Si$ plot, Fig. III). The addition of a further 3.04 (Δ Et-Me) gives the calculated B.P.N. of $PhEtHSi-$, 27.05, which compares not too unfavorably with the observed value of 28.5. Further indications of the applicability of Δ values for a fully unsymmetrical silyl group is shown by $EtMe_2Si$ (14.85) and $EtMeHSi$ (12.87) which give Δ Me-H as 1.98. The previously derived value (from the series Me_nH_{3-n}) is 1.72.

Although L. and N. did not extend their studies to compounds containing oxygen, fluorine and ethoxy substituted silyl groups, values for such groups are included in Table IX as they appear to present no correlation difficulties, although the $(EtO)_nMe_{3-n}Si-$ groups have almost the same value as the corresponding $Et_nMe_{3-n}Si-$ groups. Also the FMe_2Si- group value at 10.52 satisfies all observed data. By the interpolation process the F_2MeSi- and F_3Si- groups have values of 9.51 and 8.50, respectively, but it is possible that the high electronegativity of fluorine may invalidate these values especially for the F_3Si- group. At the present it is not possible to confirm this.

The most important feature of the trisilanes, as a consequence of the linear plots for the homologous series (Fig. I and II), is to illustrate that the value of the $R^1R^2R^3Si^L-$ group remains the same whether it is bonded to a silicon atom of the type Si^CR_3 or $Si^CR_2-SiR_3$. The superscript for the Si atoms is best explained with reference to a branched chain compound where the distinction between the different types of silicon is more obvious. The com-

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FIG. III

Legend:
- $\otimes$ $Me_nPh_{3-n}Si$
- $\odot$ $Me_nEt_{3-n}Si$
- $\square$ $Me_nCl_{3-n}Si$
- $\odot$ $Me_nH_{3-n}Si$

B.P.N.

80

70

60

50

40

30

20

0   1   2   3

$\dfrac{n}{15a}$
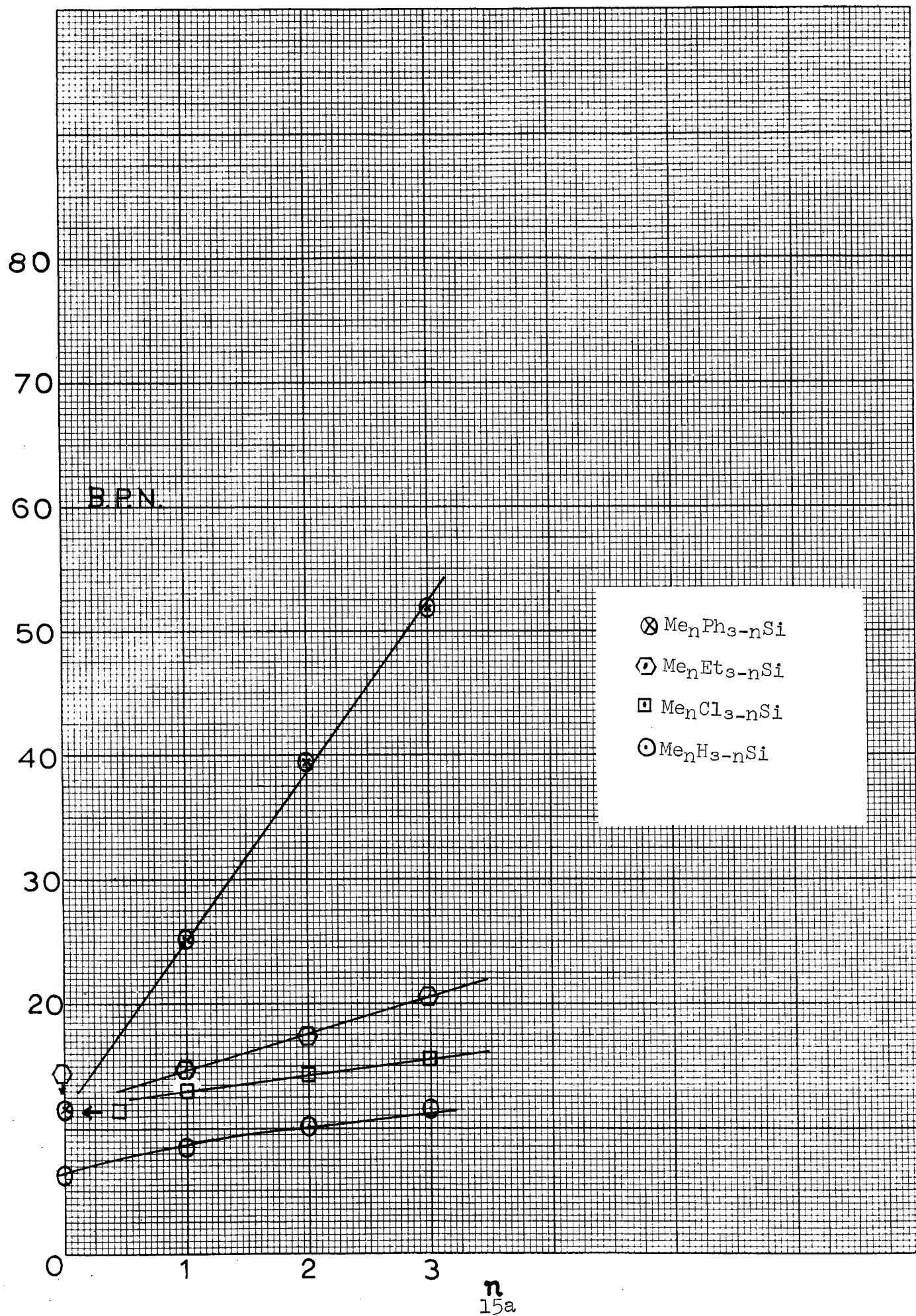
pound $(R_3Si)_4Si$ contains four "Ligand" silyl groups R_3Si^L and a "Central" silicon atom, Si^C. It is also useful to abbreviate the $R^1R^2R^3Si^L$ group to L, as in Table XIV. However, the B.P.N. value of the silylene unit $-Si^CR_2-$ is slightly varied according to the nature of the L end group as was indicated by the studies on the homologous series containing the dimethylsilylene unit, B.P.N. values for which are tabulated (Table VIII). Table XII gives additional indications of the B.P.N. value for unsymmetrical silylene units. Unfortunately, compounds containing more than one of the latter type of silylene unit are not at the present time available, and until they are the values quoted in this table can only be preliminary assignments.

A preliminary calculation for tetrakis- and tris-silyl silanes (i.e. branched chain compounds of the type $(R^1R^2R^3Si^L)_4Si^C$ and $(R^1R^2R^3Si^L)_3Si^CR$) shows that the B.P.N. of $R^1R^2R^3Si^L$ (L) decreases as the number of Si^L-Si^C bonds increases (the nomenclature was explained on page 16). In view of the restricted amount of data available (especially for reliable b.p.'s measured at an easily determined pressure) for these branched chain compounds it is of interest to investigate first of all using L. and N.'s data, the trends in change of B.P.N. with the extent of substitution of the monosilanes. We find (Fig. IV) that a linear relationship holds only for the Me and n-Pr series whereas the Et and Ph series give two different forms of a curve. Since we have already ascertained that the $R^1R^2R^3Si^L$ silyl group has the same value in the two environments $R^1R^2R^3Si^L-Si^CR_3$ and $R^1R^2R^3Si^L-Si^CR_2-SiR_3$ it appears that a relationship similar to that of the Ph series might exist, and that the B.P.N. of the ligand silyl group is only noticeably diminished in the branched chain compounds. In fact when L is $SiMe_2H$, the value for L in a tris compound is almost as low as it is in the tetrakis compound. Unfortunately, data for other ligands is not available and a comparison would be interesting. Table XIII summarizes the present situation for the branched chain polysilanes, and Table XIV gives the L assignments as far as is possible. Column 1 gives the only four silyl groups for which there is information. Columns 2-4 are headed by a formula indicating the particular environment of L for each of the columns. Column 2 gives the values of L in disilanes and higher linear homologues. Column 3 similarly gives the B.P.N. values of L in trisilylsilanes which contain an Si^CR group, and Column 4 gives L values in tetrasilylsilanes. For use in conjunction with these L values it is necessary to know also the B.P.N. values of Si^CR_3, $-Si^CR_2$, Si^CR and

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Table XII

Compound	Trisilanes b.p. °C/mm.	Ref.	b.p. °C/760 mm.	Observed B.P.N.	Silylene B.P.N.	B.P.N. Table VIII
HMe$_2$Si·SiMe$_2$·SiMe$_3$	61/22	21	165	29.1	7.26	
Me$_3$Si·SiHMe·SiMe$_3$	59/21	21	163	28.8	6.74	
HMe$_2$Si·SiMe$_2$·SiMe$_2$H	54/22	21	161	28.65	8.03	8.40
Me$_3$Si·SiMe$_2$·SiMe$_3$	175-176/760	11,12	175-176	30.38	7.32	7.70
PhMe$_2$Si·SiMe$_2$·SiMe$_3$	142/23	21	259	42.35	5.70	
Me$_3$Si·SiMePh·SiMe$_3$	133/19	21	255	41.7	18.64	
Me$_3$Si·SiMePh·SiMe$_3$	111/2.7	27	276	45.05	21.99	
ClMe$_2$Si·SiMe$_2$·SiMe$_3$	84/21	21	192	32.6	7.55	
Me$_3$Si·SiMeCl·SiMe$_3$	80.5/20	21	189	32.1	9.04	
Me$_3$Si·SiPhH·SiMe$_3$	75-80/0.55	38	265	43.3	20.44	
Me$_3$Si·SiPh$_2$·SiMe$_3$	105.5-106/0.2	61	323	53.25	30.19	
PhMe$_2$Si·SiMe$_2$·SiMe$_2$Ph	120-122/0.15	27	350	58.5	8.26	
HMe$_2$Si·SiMeBu·SiMe$_2$H	82/5.5	18	223	36.9	16.28	

FIG IV

Number of R Groups 17a
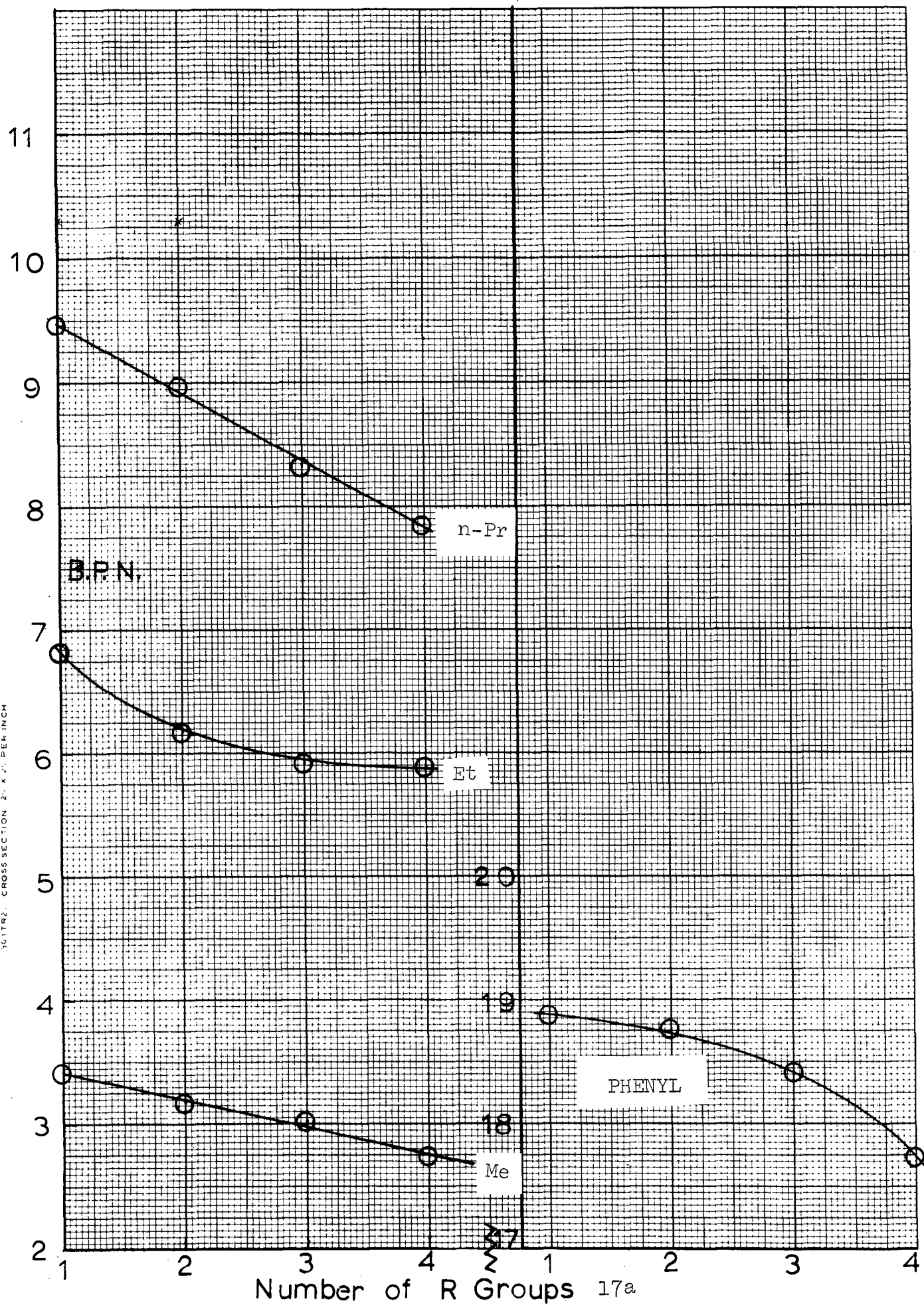
Table XIII

Branched-chain polysilanes

	b.p. °C/mm.	Ref.	b.p. °C/760 mm.	B.P.N. Obsvd.	B.P.N. Calcd.	Calcd. b.p. °C/760 mm.
(HMe₂Si)₄Si	77/1.4	18	249	40.85	40.85	249
(HMe₂Si)₃SiSiMe₂Ph	110/.01	18	385	65.60	51.89	316
(HMe₂Si)₃SiSiMePh₂	153/.016	18	455	81.5	71.24	411
(HMe₂Si)₃SiSiMePhH	115/0.3	18	337	56.0	55.85	336
(Me₃Si)₄Si	sublimes	61				205.5
(HMe₂Si)₃SiMe	68/5.2	18	205	34.30	34.32	194
(HMe₂Si)₃SiH +	60/5.0	18	195	33.0	32.85	235
(Me₃Si)₃SiMe	94–96/7	60	235	38.65	38.65	208
(Me₃Si)₃SiH	80–83/8	60	214	35.5	34.68	330
(Me₃Si)₃SiPh +	140/0.05	38	404	69.6	54.45	254
(Me₃Si)₃SiCl	70–72/0.5	62	251	41.1	40.88	380
(PhMe₂Si)₃SiH +	130/.07	63	380	64.7	64.7	
(HMe₂Si)₆Si₂	sublimes	18				
(HMe₂Si)₅Si₂Me +	110–120/.04	18	361	60.7	60.34	360

†Distillation is hampered by solidification of distillate.

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<u>Table XIV</u>

<u>B.P.N. Values of L</u>

Column 1	Column 2	Column 3	Column 4
L	$L\text{-}Si^CR_3$ and $L_2\text{-}Si^CR_2-$	L_3Si^CR	L_4Si^C
HMe_2Si	10.31	9.44	9.34
Me_3Si	11.53	11.05	11.0?
$PhMeHSi$	24.01	24.01?	24.01?
$PhMe_2Si$	25.12	20.05	?

Si^C, respectively. The values of Si^CR_3 and Si^CR_2 have already been described in Table IX and Tables VIII and XII, respectively, and Si^C is the atomic B.P.N. of Si, 3.82. The value of Si^CR is known only definitely for R = Me and R = H, and so it is necessary to investigate the relationship between B.P.N. and n for the Si^CMe_{3-n} and Si^CH_{3-n} series in order to predict other Si^CR_n values.

Table XV shows the observed values of Si^CMe_{3-n} where $3 \geqslant n \geqslant 0$, and these values are plotted in Fig. V. They fall on a curve thus giving slightly lower values than those obtained by interpolation. The interpolated values, of course, follow a linear relationship which is also found in the Si^CH_{3-n} series.

<u>Table XV</u>

<u>B.P.N. values of Si^CMe_{3-n} where $3 \geqslant n \geqslant 0$</u>

	L=SiMe₂H	L=SiMe₃	Interpolation Values
Me_3Si^C	11.53	11.53	11.53
Me_2Si^C	8.55	7.6	9.0
$MeSi^C$	6.05	5.55	6.45
Si^C	3.82	3.8	3.8

	L=any silyl group		
H_3Si	6.06		
H_2Si	5.25		
HSi	4.52		
Si	3.82		

Since the Si^CMe_{3-n} values are only slightly less than those obtained by interpolation, the latter process has been used in predicting other silylene and silylidene group B.P.N. values (see Table XVI).

Table XVI

Predicted B.P.N. values of silylene and silylidene groups

Cl_2Si,	11.64	Ph_2Si,	30.19^a	Et_2Si,	14.5
$ClSi$,	7.73	$PhSi$,	14.2	$EtSi$,	9.0

(a) observed value where $L = SiMe_3$

In conclusion, some illustrative calculations will be given for some as yet unknown polysilanes.

(a) $HMe_2Si(SiMeBu)_2SiMe_2H$

The B.P.N. for HMe_2Si is 10.31 (Table IX); and the B.P.N. for $-SiMeBu-$ is 16.28 (Table XII). Therefore, the calculated B.P.N. for the compound is 2 (10.31) + 2 (16.28) = 53.18, and the b.p. °C/760 mm. is 323.

(b) $Me_3Si \cdot (SiHMe)_3SiMeH_2$

The B.P.N. for Me_3Si is 11.53 (Table IX); the B.P.N. for H_2MeSi is 8.51 (Table IX); and the B.P.N. for $-SiHMe-$ is 6.74 (Table XII). Therefore, the calculated B.P.N. for the compound is 11.53 + 8.51 + 3 (6.74) = 40.26, and the b.p. °C/ 760 mm. is 245.5.

(c)
$$
\begin{array}{c}
SiMe_2H \\
| \\
Me_3Si-Si-Et \\
| \\
SiPhMeH
\end{array}
$$

The B.P.N. for Me_3Si is 11.05 (Table XIV);
HMe_2Si is 9.44 (Table XIV);
$HMePhSi$ is 24.01 (Table XIV);
and for Si^CEt is 9.0 (Table XVI).
Therefore, the calculated B.P.N. for the compound is 11.05 + 9.44 + 24.01 + 9.0 = 43.50, and the b.p. °C/ 760 mm. is 265.

III.   TETRAKIS(TRIMETHYLSILYL)SILANE

Since the first reported preparation of a branched chain organopolysilane,[64] several efforts have been made to synthesize tetrasilyl-substituted silanes.[64,65] Tris(triphenylsilyl)silane (4.4%) was obtained from the reaction of trichlorosilane with triphenylsilyllithium.[64] The attempted synthesis of tetrakis(triphenylsilyl)silane by the reaction of triphenylsilyllithium and silicon tetrachloride only afforded hexaphenyldisilane (72%) and a yellow oil.[64]   We now report the preparation of tetrakis(trimethylsilyl)silane, $(Me_3Si)_4Si$, (I).

In a typical procedure, 94.18 g. (0.864 mole; 20% molar excess) of chlorotrimethylsilane was dissolved in 200 ml. of sodium-dried tetrahydrofuran, to which 15.13 g. (2.15 g.-atom; 50% g.-atom excess) of lithium wire was added. To this rapidly stirred mixture, 20 ml. of a solution of 30 g. (0.18 mole) of silicon tetrachloride dissolved in 150 ml. of sodium-dried tetrahydrofuran was added at room temperature.[66] After stirring at room temperature for four hours, the reaction mixture became dark brown and heat was evolved. At this stage, drop-wise addition of the silicon tetrachloride solution was continued. Upon completed addition, the mixture was stirred overnight at room temperature. Unreacted lithium metal, some salts, and a brown polymer[67] were separated by filtration of the reaction mixture prior to hydrolysis with 200 ml. of 15% hydrochloric acid. The organic layer was separated, dried over anhydrous sodium sulfate, and the organic solvents were distilled under reduced pressure. To the yellow semi-solid residue was added a few milliliters of 95% ethanol. The solids were filtered from the ethanolic solution and purified by sublimation at 75° (0.01 mm.) giving 40.5 g. (70%) of I, m.p. 261-263.[68] Gas phase chromatography on a Dow-Corning silicone grease column at 200° gave a single peak; indicative of its purity. <u>Anal.</u> Calcd. for $C_{12}H_{36}Si_5$: C, 44.91; H, 11.31; molecular weight 321. Found: C, 45.76; H, 11.22; molecular weight 319, by osmometry in benzene. The infrared spectrum of I showed no peaks indicative of Si-H, Si-OH, and Si-O-Si. N.M.R. exhibits a sharp singlet at 9.79 τ, consistent with the highly symmetrical structure. Also, it is of interest that its high melting point[69] and ease of sublimation are presumably associated with its symmetry.

FIG Ⅴ

SiR$_{3-n}$ PREDICTIONS

SiMe$_{3-n}$

· 1   L, SiMe$_2$H

2   L, SiMe$_3$

SiH$_{3-n}$

21a
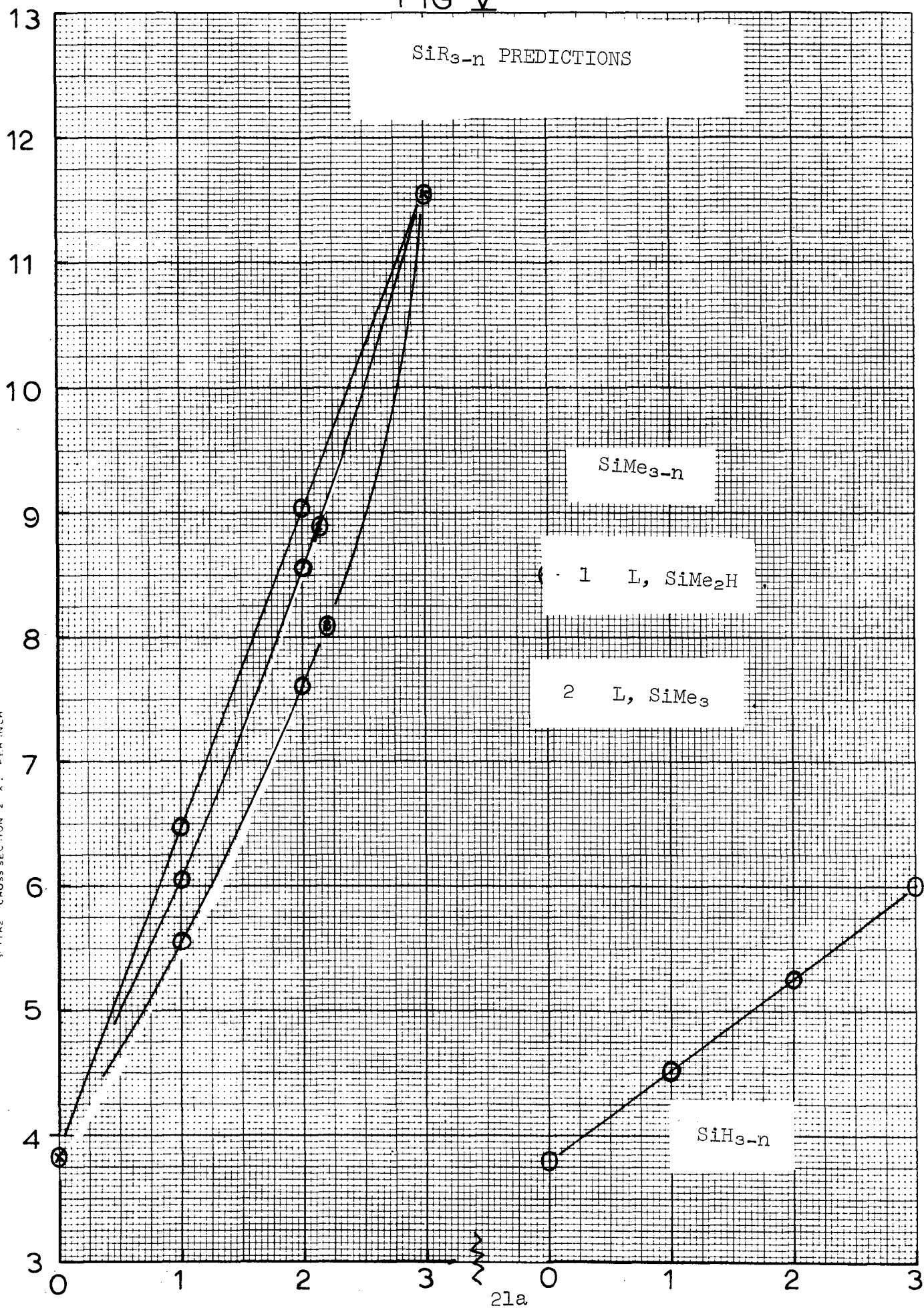
IV. POLYMETHYLATED BRANCHED-CHAIN POLYSILANYLLITHIUM COMPOUNDS. PART I: TRIS(DIMETHYLSILYL)SILYLLITHIUM AND ITS DERIVATIVES.[70]

A. Introductory Discussion

At the present time those silyllithium compounds[71] which have been characterized and which are also readily accessible have all contained at least one phenyl group, and at one time it seemed that the stability of the silyllithium moiety was dependent on the presence of the phenyl group(s). Such an observation was inevitable in view of unsuccessful attempts to prepare and isolate trialkylsilyl-alkali metal compounds. The cleavage[72] of 1,1,1-triethyl-2,2,2-triphenyldisilane by lithium in tetrahydrofuran (T.H.F.) followed by acid hydrolysis gave a low yield of triethylsilane and hexaethyldisilane in addition to triphenylsilane indicating that triethylsilyllithium was one of the intermediates.[72] Similarly the formation of trimethylsilylpotassium[26] was indicated by the isolation of trimethylphenylsilane in low yields together with tetraphenylsilane, when the cleavage products of 1,1,1-trimethyl-2,2,2-triphenyldisilane and sodium-potassium alloy were treated with bromobenzene. More recently mixtures of alkyl silyl- and silanylalkali-metal compounds have been made from dodecamethylcyclohexasilane[73] and sodium-potassium alloy. These were derivatized with trimethylchlorosilane and gave straight-chain polysilanes Si_nMe_{2n+2}, where n =2 through 5. Corresponding results were obtained by treatment of the alkali-metal compounds with methyl iodide or bromobenzene. The cleavage of dodecamethylcyclohexasilane by methyllithium[74] in ether-THF has also been shown to give a mixture of silanyllithium compounds, as evidenced by the formation of straight-chain polysilanes subsequent to treatment with trimethylchlorosilane or trimethyl phosphate. Decamethyltetrasilane has been cleaved to give mixtures of silanylalkali-metal compounds.[75] The following reaction paths have been proposed to account for the variety of products.

$$Me_{10}Si_4 \nearrow 2Me_5Si_2M$$
$$\searrow Me_3SiM + Me_7Si_3M$$

$$\xrightarrow{Me_3SiCl} \quad Me_6Si_2 \quad Me_8Si_3 \quad Me_{10}Si_4$$

$$Me_{10}Si_4 + Me_5Si_2M \longrightarrow \begin{cases} Me_7Si_3M + Me_8Si_3 \\ Me_5Si_2M + Me_{10}Si_4 \\ Me_3SiM + Me_{12}Si_5 \end{cases}$$
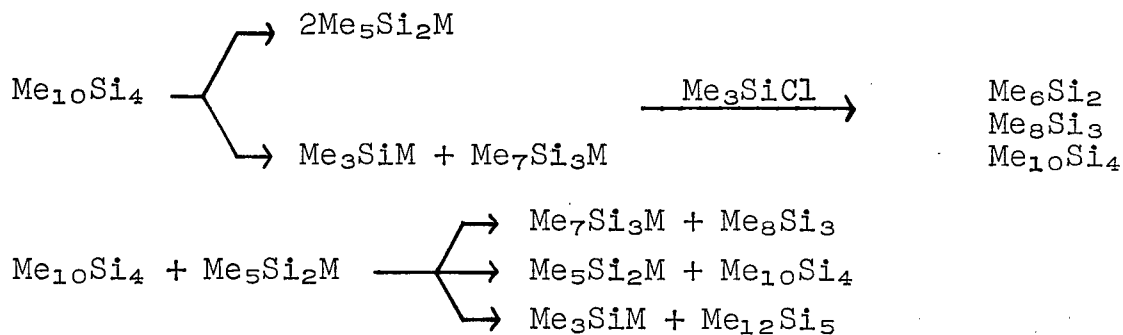
The first report of individual stable permethylated poly-silanyllithium moieties was the description[70] of the branch-chain species $(RMe_2Si)_3SiLi$ where R=Me or R=H. This dis-cussion is restricted to the case where R=H.

B. Preparation and reactions of tris(dimethylsilyl)silyl-lithium, $(HMe_2Si)_3SiLi$ (I).

I was prepared from tetrakis(dimethylsilyl)silane(II) by treatment with methyllithium in either ether or an ether-THF mixture. In the former case a milky white silyllithium mixture was obtained and the mixture containing THF was pale yellow with a smaller amount of visible white suspension. II was prepared by a method similar to that used for the preparation of tetrakis(trimethylsilyl)silane.[61] I gave a crimson upper phase for Color Test I,[76] which at the present time appears to be characteristic for compounds of the type $(RMe_2Si)_3SiLi$. The formation of the red color contrasts the usual green color obtained in a normal positive Color Test I.[76] As it has been demonstrated that polysilanes absorb ultraviolet radiation,[77] it is very likely that the chromophoric silicon skeleton of the substituted Malachite Green $\angle(p\text{-}Me_2N \cdot C_6H_4)_2 C \cdot Si(SiMe_2R)_3 7^+ I^-$ changes the usual absorption region of the dye. I can be determined by the double titration procedure[78] with allyl bromide, and in this manner the yield of the active species was shown to be 90%. Furthermore, the amount of the silyllithium did not decrease below this value during two days at 25°C. Alkylation[79] of the Si-Li group proceeded normally, and treatment with trimethyl phosphate and triiso-butyl phos-phate gave tris(dimethylsilyl)methylsilane (III) (52%) and tris(dimethylsilyl)iso-butyl silane(IV) (70%). The iso-lation of the cleavage fragment trimethylsilane, Me_3SiH,

$$\underset{\overset{|}{SiMe_2H}}{\overset{\overset{SiMe_2H}{|}}{HMe_2Si\text{-}Si\text{-}SiMe_2H}} + MeLi \longrightarrow \underset{\overset{|}{SiMe_2H}}{\overset{\overset{SiMe_2H}{|}}{HMe_2Si\text{-}Si\text{-}Li}}(I) + Me_3SiH$$

$$I + (MeO)_3PO \longrightarrow \underset{\overset{|}{SiMe_2H}}{\overset{\overset{SiMe_2H}{|}}{HMe_2Si\text{-}Si\text{-}Me}}(III)$$

$$I + (\underline{i}BuO)_3PO \longrightarrow \underset{\overset{|}{SiMe_2H}}{\overset{\overset{SiMe_2H}{|}}{HMe_2Si\text{-}Si\text{-}\underline{i}Bu}}(IV)$$

23
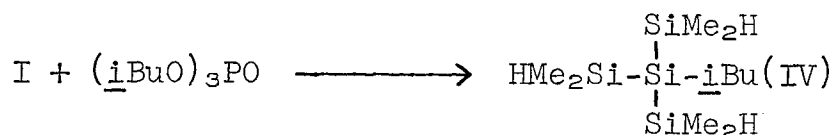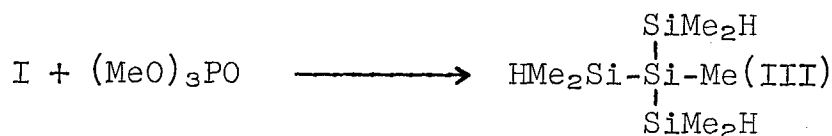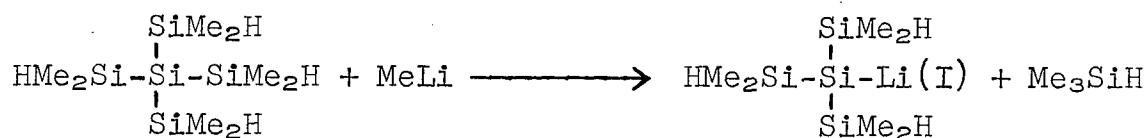
would have further substantiated the proposed reaction path.
The silyllithium(I) was also prepared from triphenylsilyl-
lithium and II, when treatment with trimethyl phosphate
gave $(HMe_2Si)_3SiMe(III)$ (36%).

$$(HMe_2Si)_4Si + Ph_3SiLi \longrightarrow (HMe_2Si)_3SiLi + Ph_3Si \cdot SiMe_2H$$

$$\downarrow (MeO)_3PO$$

$$(HMe_2Si)_3SiMe$$
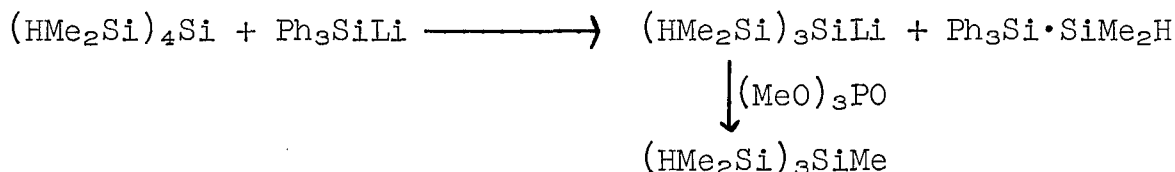
The disilane fragment 1,1-dimethyl-2,2,2-triphenyldisilane
was isolated in 26% yield.

The acid hydrolysis of I gave tris(dimethylsilyl)silane(V),
(45%) which was contaminated with some oxygen (as evidenced
by infrared spectroscopy), and the material could not be fur-
ther purified by distillation. However, by treating I with
the stoichiometric amount of a standard solution of anhydrous
hydrogen chloride in diethyl ether, a lower yield (37%) of V
was obtained in a pure form. V has also been synthesized
from the monomers by the coupling of dimethylchlorosilane
and trichlorosilane with lithium in THF.

The reaction between I and chloromonosilanes at -78°C
has given unsymmetrical tetrakis-compounds of the type
$(HMe_2Si)_3Si \cdot SiR^1R^2R^3$ where (a) $R^1=R^2=R^3=Ph$; (b) $R^1=Me$,
$R^2=R^3=Ph$; (c) $R^1=R^2=Me$, $R^3=Ph$; (d) $R^1=H$, $R^2=Me$, $R^3=Ph$;
(e) $R^1=R^2=R^3=Et$. However, an attempt to prepare an example
of compounds of the type $(HMe_2Si)_3Si \cdot SiR^1R^2 \cdot Si(SiMe_2H)_3$
where $R^1=R^2=Me$ was not successful, probably because the
appropriate technique was not employed. Molecular models
indicate packing is no more hindered in this type of molecule
than in the compound hexakis(dimethylsilyl)disilane,
$(HMe_2Si)_3Si \cdot Si(SiMe_2H)_3(VI)$ (see later). However, the
utility of I in the synthesis of higher polysilanes has
been demonstrated by the reaction between I and a monochloro-
trisilane giving a single major product, which has not yet
been fully characterized. I showed no reaction with fluoro-
benzene during 12 hours at reflux. In contrast triphenyl-
silyllithium gave a 50% yield of tetraphenylsilane under
these conditions.[71] It is notable that in no cases involving
the treatment of I with a Group IVB halide or anhydrous
hydrogen chloride did any halogen-metal interchange take
place, subsequently giving hexakis(dimethylsilyl)disilane(VI).
The latter, however, was formed by treatment of I in ether
with 1,2-dibromoethane, when a small quantity of tris(di-
methylsilyl)methylsilane(III) as well as tetrakis(dimethyl-

silyl)silane(II) was obtained. II, however, could have
been unchanged starting material. VI can be obtained
more readily by a simple modification of the procedure
for the preparation of II. By utilizing ethyl acetate
as catalyst, the amount of II is very small and the major
product is VI (ca. 30%).

C. Discussion

The accessibility and in particular the stability of
this silyllithium species raises the question concerning
its constitution. At the present time it is not unreasonable
to think in terms of a significant ionic character to the
Si-Li bond (c.f. C-Li, 43% [80]). The negatively charged
silanion is probably stabilized by charge delocalization
over the silicon skeleton. Resonance between the forms

$$
\underset{\underset{\text{SiMe}_2\text{H}}{|}}{\overset{\overset{\text{SiMe}_2\text{H}}{|}}{\text{HMe}_2\text{Si}-\text{Si}}}{}^{\ominus} \quad \longleftrightarrow \quad \underset{\underset{\text{SiMe}_2\text{H}}{|}}{\overset{\overset{\text{SiMe}_2\text{H}}{|}}{\text{HMe}_2\text{Si}-\overset{\ominus}{\text{Si}}}} \quad \longleftrightarrow \quad \underset{\underset{\text{SiMe}_2\text{H}}{|}}{\overset{\overset{\text{SiMe}_2\text{H}}{}}{\text{HMe}_2\text{Si}=\text{Si}}}{}^{\ominus}
$$
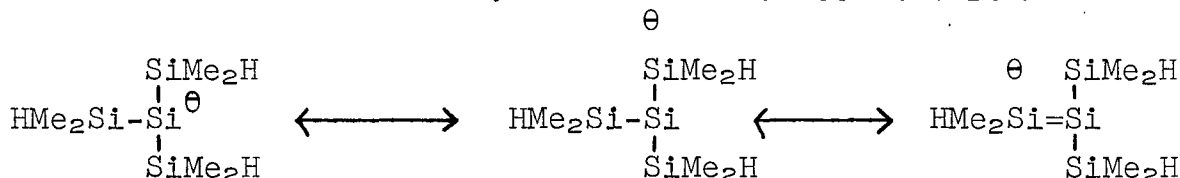
gives a decrease in ground state energy and an associated
decrease in reactivity of the silyllithium. The inferred
pseudo-conjugation invokes the participation of π orbital
overlap between silicon atoms. Whether these orbitals are
of the p or d type is not certain, although the electronic
spectrum of triphenylsilyllithium[81] has been discussed in
terms of pπ-pπ resonance between silicon and carbon atoms.
However, similar data, particularly spectroscopic evidence
for other substituted silanes have led to the conclusion
that d orbitals participate in silane conjugation.[82] Less
disputed, however, is the participation of silicon d orbi-
tals in the formation of low energy five-coordinate reaction
intermediates.[83] Also d-orbital involvement has been
suggested to be responsible for the chromophoric nature of
the silicon chain in polysilanes.[77]

It is pertinent to mention at this stage that the
preparative method for I is a unique example of the reaction
between a polysilane containing Si-H groups and a C-Li
compound. The normal reaction[84] with an alkylsilane is
$R^1R^2{}_2SiH + MeLi \longrightarrow R^1R^2{}_2SiMe + LiH$ where the Si-H
group is alkylated. However, the actual reaction for the
formation of I seems to be

$$\underset{\underset{\text{SiMe}_2\text{H}}{|}}{\overset{\overset{\text{SiMe}_2\text{H}}{|}}{\text{HMe}_2\text{Si-Si-SiMe}_2\text{H}}} + \text{Me}'\text{Li}^+ \longrightarrow \underset{\underset{\text{SiMe}_2\text{H}}{|}}{\overset{\overset{\text{SiMe}_2\text{H}}{|}}{\text{HMe}_2\text{Si-Si}'\text{-Li}^+}} + \text{Me}_3\text{SiH}$$
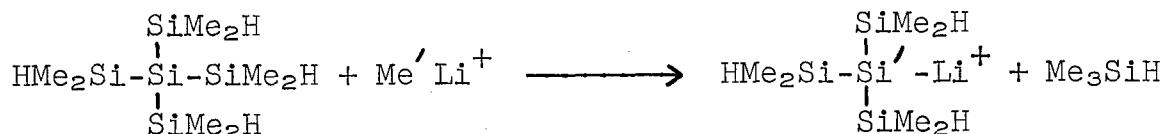
The work by Ring and Ritter[85] demonstrating that potassium hydride reacts with disilane:

$$\text{H}_3\text{Si}\cdot\text{SiH}_3 + \text{K}^+\text{H}' \longrightarrow \text{H}_3\text{SiK} + \text{SiH}_4$$
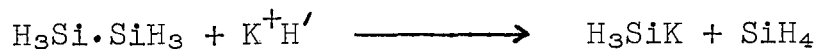
has been extended[86] to the preparation of disilanyl and trisilanyl ions:

$$\overset{+}{\text{K}}{}'\text{SiH}_3 + \underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{HSi}\cdot\text{SiH}_3}} \longrightarrow \text{K}^+{}'\text{SiH}_2\cdot\text{SiH}_3 + \text{SiH}_4$$

$$\overset{+}{\text{K}}{}^-\text{SiH}_2\cdot\text{SiH}_3 + \text{H}_3\text{Si}\cdot\text{SiH}_3 \longrightarrow \overset{+-}{\text{K}}\text{SiH}_2\cdot\text{SiH}_2\text{SiH}_3 + \text{SiH}_4$$
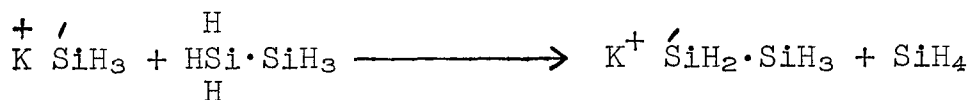
Consequently, it is possible to postulate an alternative reaction course for the formation of I. The "normal" reaction between $(\text{HMe}_2\text{Si})_4\text{Si}$ and MeLi first produces LiH;

$$(\text{HMe}_2\text{Si})_3\text{Si}\cdot\text{SiMe}_2\text{H} + \text{MeLi} \longrightarrow (\text{HMe}_2\text{Si})_3\text{Si}\cdot\text{SiMe}_3 + \text{LiH}$$

(a) $(\text{HMe}_2\text{Si})_3\text{Si}\cdot\text{SiMe}_3 + \overset{+}{\text{LiH}}{}' \longrightarrow (\text{HMe}_2\text{Si})_3\text{SiLi} + \text{Me}_3\text{SiH}$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{I}$$

(b) $\underset{}{\overset{\overset{\text{SiMe}_2\text{H}}{}}{(\text{HMe}_2\text{Si})_2\text{Si}\cdot\text{SiMe}_3}} + \overset{+}{\text{HLi}}{}' \longrightarrow \underset{}{\overset{\overset{\text{Li}}{|}}{(\text{HMe}_2\text{Si})_2\text{Si}\cdot\text{SiMe}_3}} + \text{Me}_2\text{SiH}_2$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{Ia}$$
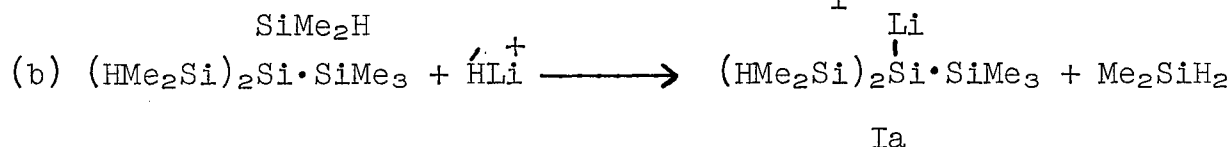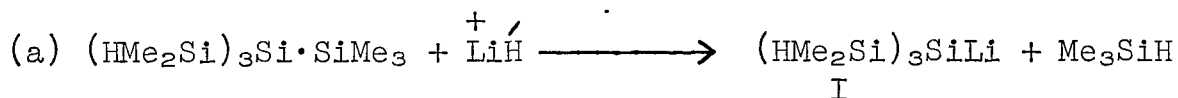
which can then react in two different ways with the intermediate $(\text{HMe}_2\text{Si})_3\text{Si}\cdot\text{SiMe}_3$. As there has not to date been any evidence for the formation of Ia it seems that the transient formation of the lithium hydride is not an important reaction, and that the Si-Li compound I is indeed formed by direct Si-Si bond cleavage by the methyllithium. Furthermore there is no evidence for reactions of the type:

$$\overset{+}{\text{Li}}{}^-\text{Si}(\text{SiMe}_2\text{H})_3 + (\text{HMe}_2\text{Si})\cdot\text{Si}\cdot(\text{SiMe}_2\text{H})_3 \longrightarrow \underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{Me}}{|}}{\text{Li}\cdot\text{Si}\cdot\text{Si}(\text{SiMe}_2\text{H})_3}}$$

$$+ (\text{HMe}_2\text{Si})_3\text{SiH}$$
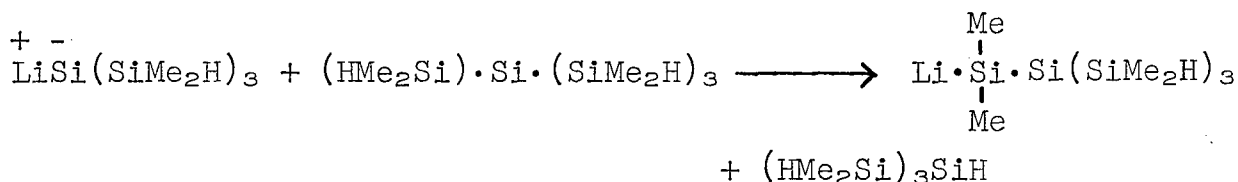
analogous to the formation of the di- and trisilanyl moieties. The treatment of II with four moles of phenyllithium has similarly been shown to effect some Si-Si bond cleavage, and the exact nature of the major product has not been ascertained. Infrared spectroscopy shows the presence of H-Si, Me-Si, and Ph-Si, and the observed b.p. in conjunction with b.p. calculations suggests the product is a disilane, probably $Si_2Ph_2Me_2H_2$ or $SiPh_2Me_3H$. Also the reaction between II and one mole of phenyllithium was shown by vapor phase chromatography (VPC) to proceed with consumption of II. Color Test I gave the pseudo-positive, red color and double titration indicated active species in 86.5% yield. After treatment with trimethyl phosphate there was obtained phenyldimethylsilane, $PhMe_2SiH$ (31.6%) and tris(dimethylsilyl)methylsilane $(HMe_2Si)_3SiMe$ (37.7%). The undistilled residue was shown by VPC to be the same as that product obtained from II and four moles of phenyllithium. One of the major reaction paths would therefore appear to involve I:

$$(HMe_2Si)_3SiSiMe_2H + PhLi \longrightarrow (HMe_2Si)_3Si^-Li^+ + PhSiMe_2H$$

$$I + (MeO)_3PO \longrightarrow (HMe_2Si)_3SiMe$$
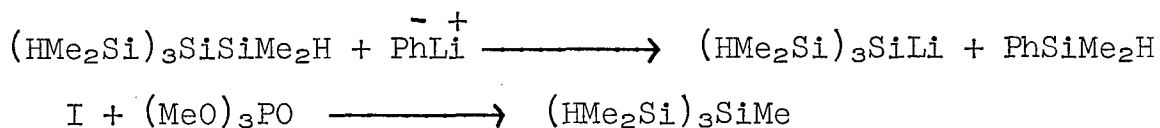
Although the cleavage of Si-Si bonds by phenyllithium is percendented,[87] straight chain polysilanes $H(SiMe_2)_nH$, where n = 4 and 6, have been shown to react normally with phenyllithium to give good yields of $Ph(SiMe_2)_nPh$ with little or no Si-Si bond cleavage.[88] In contrast to observations indicating that Si-H groups can be phenylated with phenylmagnesium bromide in THF,[84] II has shown no reaction with PhMgBr during a prolonged period.

D. Branch-chain polysilanes containing Si-H groups.

 a. Physical Properties.

 The parent pentasilane $(HMe_2Si)_4Si$(II) when freshly distilled exists as a crystalline mass m.p. 40-42°C which on agitation gives a thick slurry. All known straight-chain compounds of the type $H(Me_2Si)_nH$, where n = 2, 3, 4, 6, are all liquids illustrating that the symmetrical structure of II is responsible for its solid form. Similarly, it has been observed that the high melting point of the pentasilane, tetrakis(trimethylsilyl)silane at 261-263°C is associated with its highly symmetrical form,[61] whereas the permethylated straight-chain octa- and decasilanes have m.p.'s 60-61°C and 113-114°C, respectively.

All tetra- and pentasilane derivatives of I (Table XVII) are liquids with the exception of $(HMe_2Si)_3Si \cdot SiPh_3$ and $(HMe_2Si)_3Si \cdot SiEt_3$, which are crystallizable solids, with the former being the only compound stable to the atmosphere. All the other compounds are liquids, and those

Table XVII

Physical Properties of Branch-chain Polysilanes $(HMe_2Si)_3Si \cdot R$ Containing H-Si Groups

R	m.p. °C	b.p. °C/mm.	$n_D^{20.3}$	$d_4^{20.3}$
$SiMe_2H$	40-42	77/1.4	1.5084[a]	0.8247
$SiMePhH$	-----	115/0.3	1.5635	0.9073
$SiMe_2Ph$	-----	101/.01	1.5585	0.9101
$SiMePh_2$	-----	173/0.5	1.5940	0.9645
$SiPh_3$	135-137	sublimes	------	------
$SiEt_3$	125-128	sublimes	------	------
H	-----	60/5.0	1.4955	0.804
Me	-----	68/5.2	1.4950	0.8074
Bu^i	-----	80/2.0	1.5025	0.8381
$Si(SiMe_2H)_3$	224[b]	sublimes	------	------

a. Measurements made at 43.8°C

b. See also experimental section.

containing only the H-Si and Me-Si groups become quickly contaminated with oxygen when exposed to the air or its moisture. Consequently it is necessary for these materials to be handled under strictly anhydrous and oxygen-free conditions. The exposure to the air of most materials presents no hazard unless a large surface area is involved e.g. during the vacuum sublimation of $(HMe_2Si)_6Si_2$ (VI) a glass wool plug used as a filter in the sublimation tube (see later) ignited spontaneously on exposure to air. Pre-

27a

sumably the octasilane had coated the glass fibers thus giving exposure in a high area to weight ratio. Also if the exposing surface is cloth or paper most compounds containing H-Si and Me-Si groups only, cause a delayed ignition. Compounds containing the tertiary H-Si group i.e.

$$\text{Si-}\underset{\underset{\text{Si}}{|}}{\overset{\overset{\text{Si}}{|}}{\text{Si}}}\text{-H}$$

, however, give spontaneous ignition. Compounds of the type, (a)

$$R_3Si-\left[\underset{\underset{\text{Me}}{|}}{\overset{\overset{\text{H}}{|}}{\text{Si}}}\right]_n-SiR_3$$
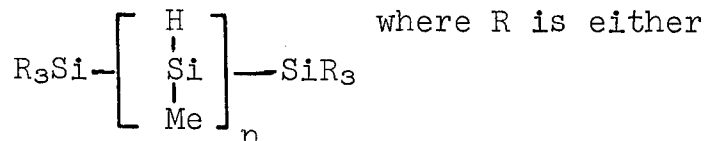
where R is either hydrogen or a methyl group and $n > 1$, and (b) $(MeHSi)_n$ where $n > 5$ have been shown to ignite when spread out in a thin layer in air.[89]

b. _Spectral Properties._

The infrared spectra of $(HMe_2Si)_4Si$, $(HMe_2Si)_6Si_2$ and $(HMe_2Si)_3SiMe$ are almost identical and the absorptions are (in microns) 3.37, 3.45 (C-H stretch), 4.76 (Si-H stretch), 7.02 shoulder on 7.06 (Me-Si antisymmetric deformation), 8.02 (Me-Si symmetric deformation), 11.30, 11.65, 12.0, 12.75 (for $(HMe_2Si)_3SiMe$ only), 13.3, and 14.35 (H-Si bending, methyl rocking and Si-C stretch). The spectrum of $(HMe_2Si)_3SiH$ is almost identical with that of $(HMe_2Si)_4Si$ except that the H-Si absorption at $4.75\,\mu$ carries a shoulder at $4.80\,\mu$, which is attributed to the tertiary H-Si group.[90] Compounds containing phenyl groups show in addition characteristic absorptions: a shoulder at 3.25 on the 3.37 peak, some weak absorptions between 5.1 and $5.7\,\mu$, and peaks at 7.0 and $9.05\,\mu$. In addition $(HMe_2Si)_3SiSiMe_2Ph$ and $(HMe_2Si)_3Si\cdot SiMePhH$ have a characteristic absorption at $12.45\,\mu$, which in $(HMe_2Si)_3Si\cdot SiMePh_2$ appears at 12.85 with a shoulder at $11.50\,\mu$. It would appear therefore that the absorption in the $12-13\,\mu$ region is characteristic of a methyl group in an environment different from that in the HMe_2Si- group. This generalization is substantiated by the absence of any such absorption in the spectra of the following compounds: $(HMe_2Si)_4Si$, $(HMe_2Si)_3SiH$, $(HMe_2Si)_3Si\cdot SiPh_3$ and $(HMe_2Si)_3Si\cdot SiEt_3$. The spectrum of the last compound is essentially the same as that of $(HMe_2Si)_4Si$, except that (a) the C-H absorptions in $3.3-3.5\,\mu$ region are more complex, (b) there are in addition, weak absorptions

at 8.95 shoulder, and 9.95 μ. Similarly the spectrum of tris(dimethylsilyl)iso-butylsilane contains in addition (a) absorptions characteristic of the iso-butyl group[91] at 7.15, 7.25, and 7.35 μ, with other absorptions at 9.20 and 9.69 μ.

The basic form of the n.m.r. spectrum of a branched chain compound containing the HMe_2Si- group is given by the symmetrical parent compound $(HMe_2Si)_4Si$ (II). The H-Si absorption of the HMe_2Si- group is a septet centered at 5.93 τ and the Me-Si absorption is a doublet at 9.69 τ, although there is a small amount of very low intensity absorption in the region. The corresponding absorptions for tetrakis(dimethylsilyl)methane,[92] $(HMe_2Si)_4C$, are similarly a septet at 5.9 τ and a doublet at 9.8 τ. Similarly the n.m.r. spectrum of hexamethyltrisilane,[21] $(HMe_2Si)_2SiMe_2$, shows the H-Si resonance of the identical HMe_2Si- groups as a septet at 6.27 τ and the Me-Si resonance is a doublet at 9.83 τ. The spectrum for hexakis(dimethylsilyl)disilane (VI) has precisely the same form as that of II, the H-Si septet is at 5.83 and the Me-Si doublet at 9.27 τ. Similarly tris(dimethylsilyl)methylsilane, $(HMe_2Si)_3SiMe$ has a septet at 6.02 τ and the doublet at 9.72 τ, though there is some low intensity absorption in this region as shoulders on the main peaks. Tris(dimethylsilyl)iso-butylsilane, $(HMe_2Si)_3Si \cdot CH_2 \cdot CH(CH_3)_2$ also shows the H-Si septet at 5.98 τ and Me-Si doublet at 9.79 τ with other absorptions attributed to the iso-butyl group between 7.95 and 9.21 τ. The spectrum of tris(dimethylsilyl)silane, $(HMe_2Si)_3SiH$ still retains the basic form, with the following modifications: (a) the primary H-Si absorption is centered at 5.95 τ, and each peak of the septet is partly resolved into a doublet, (b) the tertiary H-Si resonance is a quartet at 7.57 τ (in tris-(trimethylsilyl)silane, $(Me_3Si)_3SiH$, the tertiary H-Si resonance[90] is a singlet at 7.73 τ), (c) the Me-Si resonance is a doublet at 9.77 with some low intensity partly resolved absorptions in the immediate vicinity. There is little or no correlation between the H-Si resonance in this compound, $HSi(SiMe_2H)_3$, and the parent iso-tetrasilane,[93] $HSi(SiH_3)_3$. The asymmetry of the compound $(HMe_2Si)_3Si \cdot SiMePhH$ is indicated by the five regions of absorption. The phenyl resonance is a multiplet at 3.22 τ; the H-Si resonance of the HMe_2Si- group is a septet at 6.14 τ, whereas the H-Si resonance of the HMePhSi- group is a quartet at 5.67 τ. The Me-Si resonance of the HMe_2Si- group is the usual doublet at 9.73 τ, whereas the Me-Si resonance of the HMePhSi- is essentially a doublet at 9.41 τ.

The ultraviolet properties of straight chain compounds have been studied in some detail[77] and the absorption band λ_{max} values have been determined for the series $X(SiMe_2)_nX$ where (a) X=Me and $8 > n > 2$, (b) X=Ph and $6 > n > 2$, (c) X=Cl and n=3, 4, and 6, and (d) $X=CH:CH_2$ and n=2 and 4. Table XVIII includes some of this data with the first report of λ_{max} values for three members of the series $H(SiMe_2)_nH$.

Table XVIII

Ultraviolet Spectral Data[c] of Some Polysilanes, $X(SiMe_2)_nX$

n	X			
1	Ph[a]	Me[a]	Cl[a]	H[b]
2	236	197-199.5	---	---
3	243	215	218.5	216
4	250.5	235	235	235.5
5	257.5	250	---	---
6	265	260	259,222 shoulder	257

(a) Values for polysilanes where X=Ph, Me and Cl from ref. 77.

(b) Values reported for the first time.

(c) Spectra obtained with a Beckman DK2A Spectrophotometer using cyclohexane as solvent.

Close similarity is evident where X=Me, Cl or H and the actual λ_{max} position seems to be dependent not on the nature of the end-group but on the silicon chain length. For branched chain polysilanes λ_{max} values in general are only observed for compounds containing a phenyl group - see Table XIX.

E. Experimental

Materials: The organochlorosilanes were supplied by Dow Corning Corporation and Union Carbide Corporation. Dimethylchlorosilane was used as supplied and contained 15% of impurity consisting mainly of hydrocarbons with some tetramethylsilane and methyltrichlorosilane. THF (from DuPont), diethyl ether, and Skellysolve B (petroleum ether

Table XIX

Ultraviolet Spectral Data for Compounds of the Type $(HMe_2Si)_3Si \cdot R$, Containing the tris(dimethylsilyl)silyl Group.

R	$\lambda_{max}{}^a$ (mμ)	R	λ_{max} (mμ)
SiMe$_2$H	-----	SiMePhH	234.5, 220.3 shoulder
Si $\cdot$ (SiMe$_2$H)$_3$	-----	SiMe$_2$Ph	237
H	-----	SiMePh$_2$	236.5
SiEt$_3$	-----	SiPh$_3$	235
Me	213.5-217^b		
Bu^i	215^b		

(a) Spectrum scanned from 210 to 360 mμ.

(b) Values varied slightly according to sample concentration.

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b.p. range 60-70°C) were dried over sodium wire. Lithium, in the form of wire from Lithium Corporation, contained ⩽0.1% of sodium.

Analytical: The infrared spectra were determined in carbon disulfide solution using a Perkin Elmer Model 21 spectrophotometer. Spectra absorption intensities are abbreviated: s-strong, m-medium, w-weak, and sh-shoulder. The n.m.r. spectra were measured with a Varian HR-60 spectrophotometer operating at 60 Mcs. using carbon disulfide as solvent and cyclohexane as internal standard. Vapor phase chromatography used a column packed with silicone gum rubber SE 30 on Chromosorb W (1:20). Molecular weights were determined in benzene with a Mechrolab Vapor Pressure Osmometer Model 301A. All melting points and boiling points are uncorrected.

Apparatus: All reactions were conducted in an atmosphere of oxygen-free dry nitrogen. In view of the reactivity of most of our compounds with oxygen and water the following procedure was the method of "anhydrous work-up" subsequently referred to in the text: -

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The flask, containing the mixture of reaction product and salts in solvent, was attached to a rotary evaporator and water aspirator by means of an adaptor fitted with a tap. With the tap open, solvent was evaporated but the top was closed before removal from the evaporator spindle of the flask and adaptor. Skellysolve B and dry nitrogen were drawn into the flask to equalize the pressure and the salts were filtered off under nitrogen through a fluted filter paper which had been dried at 110°C for at least 2 days. In this way filtration has proved to be rapid and reliable without the problems of blocking associated with glass sinters. Skellysolve B was then removed from the filtrate, again using the adaptor to fill the product flask with nitrogen.

Tetrakis(dimethylsilyl)silane, (II) (0.4 mole scale).

The apparatus consisted of a four-necked, two liter, round-bottomed flask equipped with a very efficient water condenser with a nitrogen inlet, a high speed stirrer with a paddle and wire flail, a thermometer and addition funnel. To a vigorously stirred mixture of small pieces of lithium wire (24.5 gm., 0.35 mole) in THF (250 ml.) was added a mixture of silicon tetrachloride (68.0 gm., 0.4 mole) and dimethylchlorosilane (202 gm., 0.18 mole allowing for 15% impurity) in THF (200 ml) during 5 hours, to maintain a temperature of 60-65°C. The reaction mixture and lithium surface were dark brown throughout. After stirring at the ambient temperature overnight anhydrous work-up gave a pale yellow oil (80 gm.), which was distilled from a flask with a built-in Widmer column. Material boiling over the range 75-87°C/2.0 mm. was collected (58 gm., 54.5% yield). II, which had been fractionated through a glass-helices packed column (one foot long) had b.p. 77°C/1.4 mm., m.p. 40-42°C, $n_D^{43.8}$ 1.5084, and $d_4^{43.8}$ 0.8247. (Found: Si, 52.3; M.W. 273.0; M.R. 96.38. $C_8H_{25}Si_5$ requires Si, 53.0; M.W., 264.5; M.R. 96.88). The n.m.r. spectrum showed bands at 5.93 τ (H-Si) and 9.69 τ (Me-Si) with the silicon/carbon proton ratio 6.5 (calcd. 6.0). The infrared spectrum showed the following absorptions (μ): 3.37 m, 3.45 m, 4.76 s, 7.06 m, 7.02 sh, 8.0 and 8.02 doublet s, 11.31 s, 11.70 s, 12.03 s, 13.35 m, 14.35 m.

Hexakisdimethylsilyldisilane (0.2 mole scale).

The procedure was a modification of that just described for II, and involved ethyl acetate as catalyst. The chlorosilanes (the same quantities as above) in THF containing ethyl acetate (7 ml.) were added to the vigorously stirred mixture of lithium and THF containing ethyl acetate (7 ml.) to maintain a reaction temperature of 36-38°C (external cooling was required). The reaction mixture was white to pale yellow throughout, and the lithium surface was shiny to grey-white. After stirring at the ambient temperature for 12 hours, anhydrous work-up gave an oil (73.2 gm.), from which by distillation was obtained tetrakis(dimethylsilyl)silane, II, b.p. 60-70°/0.5 mm. (15.7 gm., 14.8% yield based on $SiCl_4$) which was identified by its vapor phase chromatogram and infrared spectrum. The undistilled residue (50.8 gm.) was sublimed through a temperature gradient along a horizontal tube by heating at 160°C/10^{-2} mm. and gave a hard crystalline waxy solid (handled throughout under dry oxygen-free nitrogen), hexakis(dimethylsilyl)disilane (25 gm., 30%). (Found: Si, 52.2; M.W. 406.0, 408.0. $C_{12}H_{42}Si_8$ requires Si, 54.6; M.W. 410.9). Its vapor phase chromatogram under different conditions was a single peak indicative of high purity, and its infrared spectrum was identical with that of II. Similarly, its n.m.r. spectrum was almost identical with that of II, and the H-Si septet was at 5.83τ, and the Me-Si doublet at 9.27τ. The silicon/carbon proton ratio was 6.1 (calcd. 6.0). The following observations pertain to the measurement of the m.p. in a capillary tube heated in a Mel-Temp heating block: (a) when gradually heated it softened and wetted the glass at 100-120°C but the last traces of solid did not melt until ca. 225°C; (b) a sample placed in the block at 201°C mainly melted but the remaining solid disappeared at 224°C. This temperature would therefore appear to be characteristic and is probably the true melting point.

Note: The sublimation process included the interposition of a glass wool plug between the crude material and the cooler region of tube. Its purpose was to prevent splashings or frothings from contaminating sublimate. Subsequently this plug was exposed to the atmosphere, and it almost immediately burst into flames, and thereafter burned very vigorously.

Tris(dimethylsilyl)silyllithium, I

(a) in diethyl ether.

To $(HMe_2Si)_4Si$ (12.3 gm., 4.84×10^{-2} mole) in ether (50 ml.) was added methyllithium[94] (4.84×10^{-2} mole), 435 ml. of a 1.09N ethereal solution - determined by double titration with 1,2-dibromoethane[95]) and the white milky mixture was boiled for two hours, after the initial exothermicity had subsided. VPC analysis of a hydrolyzed sample indicated that only a trace of starting material remained and that the major product had an identical retention time to that of tris(dimethylsilyl)silane (see later). Color Test I[76] gave a crimson upper phase and a colorless lower phase. Double titration with allyl bromide[78] showed that the silyllithium was formed in 90% yield to give a 0.46N solution. The concentration did not fall below this value during 2 days.

(b) in ether/THF mixture.

The only difference, from that described in (a) above was that the mixture was pale yellow with a smaller amount of visible suspension. Also (see preparation of $(HMe_2Si)_3$-$SiBu^i$) the amount of unchanged II (hydrolyzed sample - VPC) was greater than with ether as the only solvent.

Tris(dimethylsilyl)silane, $(HMe_2Si)_3SiH$, from I and anhydrous hydrogen chloride.

The silyllithium was prepared from II (10.70 gm., 4.04×10^{-2} mole) and methyllithium (41.6 ml. of a 0.97M solution) by stirring at the ambient temperature for half an hour. A solution of anhydrous hydrogen chloride in dry ether (4.04×10^{-2} mole; 126.5 ml. of a 0.32 mole solution) was added slowly and gave a copious white powdery precipitate. After 2 hours, anhydrous work-up gave a colorless liquid (5.4 gm.) which was distilled from a flask with a built-in Widmer column. Tris(dimethylsilyl)-silane, b.p. 60-64°C/5.0 mm. was the major product but the last fractions contained some tetrakis(dimethylsilyl)-silane, II. By comparison of the retention times and peak areas of the vapor phase chromatogram, the products were showen to be tris(dimethylsilyl)silane (2.7 gm., 37%) and unchanged tetrakis(dimethylsilyl)silane (1.25 gm.). In a larger scale reaction the yield of tris(dimethylsilyl)-silane was 23.4%. Freshly distilled material, b.p. 60°C/5.0 mm., was pure by vapor phase chromatographic

analysis, $n_D^{20.3}$ 1.4955, $d_4^{20.3}$ 0.804. Found: M.R. 79.0; the calculated value is 75.8. Freshly distilled material was used for the spectroscopic analysis: (a) the n.m.r. spectrum showed the primary H-Si, tertiary H-Si, and Me-Si resonances centered at 5.80, 7.37 and 9.77 τ, respectively, with the proton ratio 1:3:18.2 (calculated 1:3:18); (b) the infrared spectrum showed the following absorptions (μ): 3.38 m, 3.45 sh-m, 3.57 sh-w, 4.74 s, 4.90 sh-m, 7.22 w, 8.05 s, 11.34 s, 11.75 s, 12.0 s, 12.87 w, 13.26 m, 14.30 m, and 14.57 m.

In view of the reactivity of this compound no elemental analyses were possible, and it was characterized by correlation of b.p., infrared and n.m.r. data. When placed on adsorbent paper in the atmosphere, spontaneous ignition occurred. Slow decomposition of the tris(dimethylsilyl)silane was ascertained by VPC.

The synthesis of tris(dimethylsilyl)silane from the monomers.

The apparatus was similar to that used for the preparation of tetrakis(dimethylsilyl)silane.

To a vigorously stirred mixture of small pieces of lithium wire (4.6 gm., 0.66 gm.-atom) in THF (100 ml.) was added a mixture of trichlorosilane (13.55 gm., 0.1 mole), dimethylchlorosilane (35.0 gm., 0.3 mole allowing for the 15% impurity) and THF (250 ml.) during ca. 2 hours. The exothermic reaction was modified by external cooling. Anhydrous work-up gave an oil (16 gm.) which was distilled from a flask with a built-in Widmer column. Tris(dimethylsilyl)silane, b.p. 58-65°C/5.5 mm. was identified by its infrared spectrum and vapor phase chromatogram. The last fraction, tetrakis(dimethylsilyl)silane, b.p. 74°C/1.5 mm.-79°C/1.3 mm. was similarly identified. Intermediate fractions were mixtures, and by comparison of retention times and peak areas of the vapor phase chromatograms the reaction products were shown to be tris(dimethylsilyl)silane (2.5 gm., 12.1% yield based on $HSiCl_3$) and tetrakis(dimethylsilyl)silane (6.2 gm., 31% yield based on HMe_2SiCl).

Tris(dimethylsilyl)silane by hydrolysis of I.

After being stirred overnight the reaction mixture from tetrakis(dimethylsilyl)silane (12.1 gm., 4.56×10^{-2}

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mole) and methyllithium (47 ml. of a 0.97M solution; 4.56x10^{-2} mole) was hydrolyzed with dilute HCl and gave on work-up an oil (6.4 gm.). Distillation gave tris-(dimethylsilyl)silane, b.p. 56-60°C/5.0 mm., identified by VPC and its infrared spectrum, although Si-O was present. (Redistilled product still contained Si-O). The last fraction, tetrakis(dimethylsilyl)silane, b.p. 70-77°C/1.4 mm., was identified by its infrared spectrum and VPC. The yield of tris(dimethylsilyl)silane, 3.7 gm., was 45%, allowing for the recovered starting material.

Tris(dimethylsilyl)methylsilane, (HMe$_2$Si)$_3$SiMe from the reaction between I and trimethyl phosphate.

(a) I prepared from tetrakis(dimethylsilyl)silane (II) and methyllithium

To the silyllithium, prepared by mixing II (4.5 gm., 4.33x10^{-2} mole) in ether (20 ml.) and methyllithium (6.25x10^{-2} mole, 74 ml. of a 0.84M solution) for 20 minutes, was added trimethyl phosphate (13.1 gm., 9.35x10^{-2} mole). The reaction was exothermic and gave a copious white precipitate. Anhydrous work-up gave an oil (5.55 gm.) which on distillation gave tris(dimethylsilyl)methylsilane, b.p. 55-63°C/3.4 mm. (4.7 gm., 52%). Pure material had b.p. 68°C/5.2 mm., n$_D^{20.3}$ 1.4950, d$_4^{20.3}$ 0.8074 (Found: Si, 50.3%; M.R. 80.02. C$_7$H$_{24}$Si$_4$ requires Si, 50.9%; M.R. 80.24). The n.m.r. spectrum showed the H-Si and Me-Si resonance as a septet at 6.02 τ and a doublet at 9.72 τ, respectively, with the carbon/silicon proton ratio 7.15 (calcd. 7.0). The infrared spectrum was the same as that of tetrakis-(dimethylsilyl)silane, II, with an additional absorption at 12.75 μ, s.

(b) I prepared from II and triphenylsilyllithium.

To II (10.15 gm., 3.82x10^{-2} mole) in ether (50 ml.) was added triphenylsilyllithium (4.33x10^{-2} mole, 76 ml. of a 0.57M solution in THF-determined by the double titration procedure[78] with allyl bromide), and the reaction mixture became red-brown but did not warm up. After stirring for 4 1/2 hours at the ambient temperature titration of the silyllithium solution indicated the presence of 2.83x10^{-2} mole (74%) of an active species. Vapor phase chroma-

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tographic analysis of a hydrolyzed sample (<u>ca</u>. 1/4 ml.)
showed tris(dimethylsilyl)silane and a trace of II (by
comparison with an authentic chromatogram under the same
conditions). Color Test I[76] gave an orange-red upper
phase. To the silyllithium solution was added trimethyl
phosphate (9.1 gm., 6.50×10^{-2} mole) and after stirring
overnight anhydrous work-up gave an oil (17.1 gm.) from
which crystals (2.7 gm.) formed during 36 hours. The
supernatant liquid was distilled from a flask with a
built-in Widmer column, and gave tris(dimethylsilyl)methyl-
silane, 2.85 gm., b.p. $59°C/6.5$ mm.$-61°C/5.5$ mm., $n_D^{20.3}$
1.4930 (pure material had $n_D^{20.3}$ 1.4965) which was identi-
fied by its infrared spectrum and vapor phase chromatogram
which were identical to that of an authentic specimen.
The undistilled residue (7.85 gm.) was chromatographed on
neutral alumina and gave a white solid. This was combined
with the crystals from the curde reaction mixture and
crystallizations from methanol-ethyl acetate (4:1) gave
1,1-dimethyl-2,2,2-triphenyldisilane (3.15 gm., 26%) m.p.
92.5-93.0°C (Found: Si, 17.5%; M.W. 320, 321. $C_{20}H_{22}Si_2$
requires Si, 17.6%, M.W. 318.5). The infrared spectrum
showed the following absorptions (μ): 3.29 m, 3.32 sh,
3.38 m, 4.78 s, 5.13 w, 5.32 w, 5.50 w, 7.55 w, 7.71 w,
8.02 sh on 8.95 s, 8.43 m, 9.07 s, 9.41 w, 9.72 m, 10.02 m,
11.34 sh and 11.46 sh on 11.56 s, 11.94 s, 13.38 sh on
13.57 s, 14.22 sh on 14.36 s, and 14.95 m.

Tris(dimethylsilyl)iso-butylsilane.

(a) Using ether-THF solvent.

To II (14.9 gm., 5.63×10^{-2} mole) in THF (100 ml.) was
added methyllithium (5.63×10^{-2} mole) at 10°C. After 1/2
hour vapor phase chromatographic analysis of a hydrolyzed
sample indicated that some starting material remained in
more than trace quantity. Successive quantities of methyl-
lithium were added but some II always remained. In this
way a total amount of methyllithium (7.65×10^{-2} mole, 35.9%
excess) had been added. The silyllithium was slowly added
to freshly distilled tri<u>iso</u>-butyl phosphate (20.1 gm.,
7.65×10^{-2} mole) and turned pale orange. Anhydrous work-
up gave an oil (16.5 gm.), which was distilled through
a Widmer spiral to give 95% pure tris(dimethylsilyl)<u>iso</u>-
butylsilane b.p. $90°C/3.4$ mm. $- 93°C/3.6$ mm. (The impurity
detected by vapor phase chromatography had the same retention
time as II). Redistilled material (7.55 gm., 51%) b.p.
$94°C/3.4$ mm., still was not pure. Analytically pure

material, b.p. 80°C/2.0 mm., $n_D^{20.3}$, 1.5040, $d_4^{20.3}$ 0.8226, was obtained only after fractionation from a spinning band column. (Found: M.R. 94.58; $C_{10}H_{30}Si_4$ requires M.R. 94.16). The n.m.r. spectrum showed the following absorptions: H-Si septet at 4.02τ, Si-Bu^i multiplet at 8.05 w, 8.16 w, 8.28 w, 8.38 w, 8.50 w, 8.60 w, 8.72 w, 8.80 w, 8.98 s, 9.10 s, 9.12 sh-s, 9.22 m τ and Me-Si doublet at 9.79τ. The proton ratio was, respectively, 1:3.1:6.3 (calcd. 1:3:6). The infrared spectrum showed the following absorptions (μ): 3.38 m, 3.45 sh-m, 3.52 sh-m, 3.57 sh-w, 4.77 s, 7.17 w, 7.26 w, 7.34 w, 7.55 w, 7.60 w, 8.02, 8.04 doublet-s, 8.61 w, 9.21 w, 9.68 w, 11.30 s, 11.65 s, 12.00 s, 13.35 m, 13.70 m, and 14.35 m.

(b) **In** ether alone.

To II (38.3 gm., 14.45x10^{-2} mole) in ether (50 ml.) was added methyllithium (115 ml. of a 1.276M solution, i.e. 14.7x10^{-2} mole) and the mixture was stirred for ca. one hour after the exothermicity had subsided. To the silyllithium was added triiso-butyl phosphate (39.2 gm., 14.7x10^{-2} mole) at 25°C. The orange color of the mixture persisted but faded overnight. Anhydrous work-up gave an oil (38.6 gm.) which was distilled through a Widmer spiral to give tris(dimethylsilyl)iso-butylsilane, b.p. 81-82°C/2.0 mm. (26.75 gm., 70.0%), which was identified by its vapor phase chromatogram and infrared spectrum. The former indicated the presence of a very small amount of impurity, very probably unchanged starting material, II.

Tris(dimethylsilyl)(dimethylphenylsilyl)silane, (HMe₂Si)₃Si·SiMe₂Ph.

The silyllithium, which was prepared from II (5.25x10^{-2} mole) and methyllithium (57 ml. of a 0.925M solution - determined by double titration[78] with allyl bromide), was added slowly to phenyldimethylchlorosilane (9.9 gm., 5.78x10^{-2} mole) in ether (30 ml.) at -78°C. After stirring overnight at the ambient temperature, and anhydrous work-up, an oil was obtained. Distillation gave a liquid, tris(dimethylsilyl)(phenyldimethylsilyl)silane (11.3 gm., 63%) b.p. 101°C/0.01 mm., $n_D^{20.3}$ 1.5585, $d_4^{20.3}$ 0.9101. (Found: Si, 40.8; M.R. 120.9. $C_{14}H_{38}Si_5$ requires Si, 40.8; M.R. 121.2). The infrared spectrum gave the following absorptions (μ): 3.26 w, 3.38 m, 3.45 w, 4.76 s, 7.00 m, 7.03 sh-w, 7.07 sh, 7.11 sh, 8.02, 8.04 doublet-s, 9.05 m, 11.27 s, 11.70 s, 12.03 s, 12.45 s, 13.15 m, 13.3 sh, 13.67 m, and 14.3 s.

A subsequent larger scale preparation $(20.1 \times 10^{-2}$ mole) gave 39.1 gm. of product (58% yield), b.p. 115°C/3.0 mm.

Tris(dimethylsilyl)(methyldiphenylsilyl)silane

The silyllithium, I $(20.1 \times 10^{-2}$ mole), in ether (375 ml.) was added to diphenylmethylchlorosilane (46.6 gm., 20.1×10^{-2} mole) in ether (100 ml.) at -78°C. Anhydrous work-up gave an oil (84 gm.) from which was obtained by distillation tris(dimethylsilyl)(methyldiphenylsilyl)silane b.p. 173°C/0.5 mm. (44.5 gm., 55% yield) $n_D^{20.3}$ 1.5940, $d_4^{20.3}$ 0.9645 (Found: Si, 35.0%; M.R. 141.7. $C_{34}H_{19}Si_5$ requires Si, 34.83%; M.R. 141.2). The infrared spectrum showed absorptions (μ) at: 3.26 m, 3.30 sh, 3.38 m, 3.46 m, 3.55 sh, 4.75 s, 5.12 w, 5.30 w, 5.50 w, 5.67 w, 6.06 w, 6.30 w, 6.37 w, 6.74 w, 7.01 w, 7.07 sh, 7.52 w, 7.70 w, 8.02, 8.05 doublet-s, 8.43 w, 9.95 sh, 9.05 s, 9.10 sh, 9.40 w, 9.74 w, 10.05 m, 11.30 s, 11.69 s, 12.02 s, 12.84 s, 13.35 sh-m, 13.65 s, 14.05 s, 14.35 s, and 14.8 m. The n.m.r. spectrum for this material, where the groups are designated: $(HMe_2Si)_3Si \cdot SiMePh_2$ were:- A septet 5.77 τ,

$$\begin{matrix} | \; | & & | \; | \\ A \; B & & C \; D \end{matrix}$$

B doublet 9.87 τ, C singlet 9.29 τ, and D a multiplet at 2.72 τ. The ratio was 1.0:6.0:1.06:3.5 (calcd. 1:6:1:3.33).

A smaller scale preparation $(4.45 \times 10^{-2}$ mole) gave 12.6 gm., 70% yield, b.p. 153°C/0.016 mm., $n_D^{20.2}$ 1.5940.

Tris(dimethylsilyl)triphenylsilylsilane

The silyllithium $(4.45 \times 10^{-2}$ mole) was added to triphenylchlorosilane $(5.34 \times 10^{-2}$ mole) at -78°C. Anhydrous work-up gave a hard, white wax (26.3 gm.). Repeated crystallization from methanol-ethyl acetate (4:1) gave tris(dimethylsilyl)(triphenylsilyl)silane, m.p. 135-137.5°C (7.0 gm., 34%) (Found: Si, 29.50. $C_{39}H_{21}Si_5$ requires Si, 30.18). The infrared absorptions were as follows (μ): 3.27 m, 3.38 m, 3.45 m, 4.76 s, 7.00 m, 8.0 sh-m, 8.04 m, 8.40 w, 8.65 w, 9.07 m, 9.71 w, 10.1 w, 11.30 s, 11.70 s, 12.00 s, 13.59 m and 14.34 s.

Tris(dimethylsilyl)(methylphenylsilyl)silane, $(HMe_2Si)_3Si \cdot SiMePhH$

The silyllithium $(9.85 \times 10^{-2}$ mole) was added to methylphenylchlorosilane (16.0 gm., 9.85×10^{-2} mole) at -78°C.

Distillation of the oil obtained from anhydrous work-up
gave tris(dimethylsilyl)(methylphenylsilyl)silane (19.0 gm.,
60%) b.p. 115°C/0.3 mm., $n_D^{20.3}$ 1.5635, $d_4^{20.3}$ 0.9073 (Found:
Si, %; M.W. 320, 321; M.R. 117.0. $C_{13}H_{30}Si_5$ requires
Si, 42.9%; M.W. 327; M.R. 116.82). The infrared spectrum
showed the following absorptions (μ): 3.27 w, 3.37 m,
3.44 w, 4.76 s, 7.00 m, 7.06 sh-w, 8.02, 8.04 doublet-s,
9.03 m, 11.30 s, 11.68 s, 12.00 s, 12.45 s, 13.35 w-broad,
13.75 w-broad, 14.15 m, and 14.36 m. The n.m.r. spectrum
for the material designated as: $(HMe_2Si)_3Si\cdot SiMePhH$ were:

$$ \underset{A\ \ B}{(HMe_2Si)_3Si} \cdot \underset{B'\ C'\ A'}{SiMePhH} $$

A septet at 6.14 τ, A a quartet at 5.67 τ, B a doublet
at 9.73 τ, B a doublet at 9.41 τ, and C a multiplet at
3.22 τ, with the ratio 2.85:1.0:17.0:3.0:5.0 (calcd.
3:1:18:3:5).

Tris(dimethylsilyl)(triethylsilyl)silane, $(HMe_2Si)_3Si\cdot SiEt_3$

To freshly distilled triethylfluorosilane (9.55 gm.,
7.1×10^{-2} mole) at -78°C was added I (6.0×10^{-2} mole). An-
hydrous work-up gave a crystalline mass (16.45 gm.). Sub-
limation along a horizontal tube (handling throughout was
under dry nitrogen) gave a white, hard, waxy crystalline
solid, tris(dimethylsilyl)(triethylsilyl)silane, (16.0 gm.,
84% yield) m.p. 125-128°C which could be crystallized from
methanol-ethyl acetate (4:1). (Found: Si, 44.0%,
$C_{12}H_{36}Si_5$ requires Si, 43.75%). The infrared spectrum
showed the following absorptions (μ): 3.38, 3.45, 3.47
triplet-s, 4.77 s, 7.21 sh on 7.26 m, 8.02 sh on 8.06 s,
8.50 w, 8.76 w, 9.84 sh on 9.95 m, 10.43 broad-w, 11.35 s,
11.70 s, 12.03 s, 13.45 m, and 13.85 m. The n.m.r. showed
the H-Si resonance as a septet at 5.56 τ, the Me-Si resonance
as a doublet at 9.73 τ, and the Et-Si resonance as a multi-
plet between 8.86 and 9.47 τ. The proton ratio was
1.0:6.3:5.1 (calcd. 1:6:5).

Attempted preparation of $[(HMe_2Si)_3Si]_2SiMe_2$

To the silyllithium I (9.55×10^{-2} mole) at the ambient
temperature dichlorodimethylsilane (3.34 gm., 2.5×10^{-2} mole)
in diethyl ether (50 ml.) was added slowly during 20 minutes
and caused mild reflux. The reaction mixture was pale
yellow after being boiled overnight. After the addition
of trimethyl phosphate (14.85 gm., 10.5×10^{-2} mole), an-
hydrous work-up gave an oil (ca. 25 ml., 18.7 gm.), which

was distilled from a flask with a built-in Widmer spiral
and gave ten fractions: 1) 0.75 gm., 66°C/8.0 mm.,-75°C/
4.5 mm., 2) 2.8 gm., 78°C/4.5 mm.-90°C/4.1 mm., 3) 2.5 gm.,
90°C/4.1 mm.-78°C/1.1 mm., 4) 2.0 gm., froths to 105°C/
0.2 mm., 5) 0.2 gm., 105°C/0.25 mm., 6) 1.2 gm., 90°C/0.004
mm. (bath at 160°C), 7) 0.1 gm.,90°C/0.004 mm.,very low drip
rate, 8) 0.6 gm., 135°C/0.005 mm., 10) 1.20 gm., 150°C/
0.005 mm.; residue 1.85 gm. Vapor chromatographic analysis
allows the following conclusions to be made: II (3.05 gm.,
1.10×10^{-2} mole) was recovered and therefore 8.45×10^{-2} mole
had reacted giving I. This was treated with Me_2SiCl_2
(3.34 gm., 2.5×10^{-2} mole) which would consume 5.00×10^{-2}
mole of I. The excess of I was derivatized with trimethyl
phosphate and a 100% yield from this excess would have been
$(HMe_2Si)_3SiMe$, 7.6 gm., 3.45×10^{-2} mole. In fact $(HMe_2Si)_3SiMe$,
4.35 gm., 1.98×10^{-2} mole, 57% was obtained. A 100% yield
of the required nonasilane would have been 11.7 gm.; however,
three high boiling products, previously detected by VPC in
the crude reaction mixture, were isolated, none of which
was pure. However, VPC enabled the % composition of each
fraction to be computed and the overall quantity of each
component was 1.0, 2.4, and 0.9 gm., respectively. The
boiling point of 150°C/0.005 mm. was equivalent to ca.
450°C/760 mm. The required nonasilane had a calculated
b.p. of 380°C/760 mm. The mixture of high boiling products
had a λ max in the ultraviolet at 242.5 mμ. Permethylated
polysilanes $Me(SiMe_2)_nMe$ where n = 3, 4, 5, and 6 have
λ max values of 215, 235, 250, and 260 mμ, respectively.[77]
The nonasilane being branched would have, however, five
members in its longest chain.

Attempted preparation of $(HMe_2Si)_3Si \cdot SnMe_3$

After I (3.99×10^{-2} mole) was boiled for 1 hour, tri-
methyltin(IV) chloride (8.8 gm., 4.39×10^{-2} mole, 10% excess)
was added, and the mixture boiled overnight. Anhydrous
work-up gave an oil (13.3 gm.). Attempts at distillation
through a Widmer spiral gave small amounts of distillate,
and into the column sublimed a solid which was shown by VPC
to contain three components. Sublimation effected no sepa-
ration and the material was moisture sensitive.

The coupling of I with 1,2-dibromoethane to give hexa-kis(dimethylsilyl)disilane.

To I (4.45×10^{-2} mole) in ether (100 ml.) was added
1,2-dibromoethane (freshly distilled) (4.62 gm., 2.45×10^{-2}

mole, 10% excess) in ether (50 ml.) during 20 minutes.
There was no noticeable evolution of gas but the mixture
warmed and turned bright orange. Color Test I[76] gave a
red upper phase, i.e. it was pseudo-positive. The addi-
tion of further 1,2-dibromoethane (1.6 gm.) turned the
mixture white and Color Test I was negative. Anhydrous
work-up gave an oil (9.55 gm.). Distillate, b.p. 60°C/
5.5 mm.-74°C/5.5 mm. was mainly tris(dimethylsilyl)methyl-
silane (ca. 3.0 gm., identified by VPC), and the distillate
with b.p. 75°C/1.8 mm.-70°C/1.6 mm. was mainly tetrakis-
(dimethylsilyl)silane (ca. 2.0 gm., identified by VPC).
Some of the undistilled residue (3.8 gm.) was sublimed into
the column giving a white semi-crystalline waxy solid which
had the same vapor phase chromatogram as an authentic speci-
men of hexakis(dimethylsilyl)disilane. By comparing the
peak area of the vapor phase chromatogram of a standard
solution of hexakis(dimethylsilyl)disilane and the peak
area of a solution of the undistilled residue, the latter
was shown to contain 2.0 gm., 23% of hexakis(dimethylsilyl)-
disilane.

The reaction between II and four moles of phenyllithium

in ether

To II (3.5 gm., 1.33×10^{-2} mole) was added phenyllithium
(76 ml. of an 0.712N solution in ether - determined by double
titration[78] with allyl bromide) and the mixture was stirred
at 35°C for five hours, and at 25°C for twelve hours before
hydrolysis with dilute hydrochloric acid to give an oil
(5.85 gm.). Distillation in a specially designed small
scale apparatus gave 4.10 gm. of a liquid, of which the
fraction b.p. 81-82°C/0.025 mm. was quite pure. Found:
$n_D^{20.3}$ 1.5500, M.W. 234, 237, and extrapolated b.p. 340°C.
For $Si_2Ph_2Me_2H_2$: M.W. 232, calculated b.p. 312°C and
for $Si_2Ph_2Me_3H$, M.W. 256, calculated b.p. 329°C. The in-
frared spectrum showed absorptions attributed to H-Si, Me-Si,
and Ph-Si groups at 4.75, 8.0 and 9.0 μ, respectively.

The reaction between II and one mole of phenyllithium

II (9.6 gm., 3.62×10^{-2} mole) in ether (50 ml.) was
treated with phenyllithium (52 ml. of an 0.8N solution,
4.16×10^{-2} mole, 18% excess). The mixture warmed but did
not boil and soon became milky. It was boiled for 1 3/4
hours, when Color Test I gave an orange-red upper phase,
and a double titration with allyl bromide[78] indicated that
the mixture contained 3.12×10^{-2} mole of an active species
(86.5% based on II; 75% based on phenyllithium). A
hydrolyzed sample was shown (VPC) to contain only a trace

of II, as well as other components to be mentioned. The reaction mixture was treated with trimethyl phosphate (8.55 gm., 6.14×10^{-2} mole, 50% excess over phenyllithium) and after stirring at the ambient temperature overnight, anhydrous work-up gave an oil (11.0 gm.) which was distilled from a flask with a built-in Widmer spiral. By VPC the fractions were analyzed: 1) b.p. 55°C/19 mm.-59°C/16 mm. mainly phenyldimethylsilane, 2) b.p. 59°C/6 mm.-84°C/16 mm. 65% phenyldimethylsilane and 35% tris(dimethylsilyl)methylsilane, 3) 84-87°C/15 mm. $n_D^{20.3}$ 1.4955 pure tris(dimethylsilyl)methylsilane. The undistilled residue (2.3 gm.) contained as the only volatile component that compound formed from the previous reaction. The overall amounts of each compound were: phenyldimethylsilane (1.58 gm., 31.6%) and tris(dimethylsilyl)methylsilane (3.00 gm., 37.7%).

The reaction between I and 1H,3-chlorohexamethyltrisilane.[96]

The silyllithium(I) (6.00×10^{-2} mole) in ether was added to 1H,3-chlorohexamethyltrisilane (12.40 gm., 5.88×10^{-2} mole) at -78°C. After stirring overnight anhydrous work-up gave an oil (17.0 gm.). VPC analysis showed the major product as a single peak at 3.45 cm. at 200°C. Only very small amounts of lower boiling components were present. The purification of the product is as yet incomplete.

V. PREPARATIONS AND REACTIONS OF HETEROCYCLIC POLYSILANES

A. Discussion

Several organically substituted cyclosilanes have been prepared. The known compounds are tetra-, penta- or hexacyclic and are represented by structures Ia[97,98] Ib[99], IIa,[97,100] IIb[101], IIc[99], IIIa[38], IIIb[102] and IIIc[103,73,104]. A recent review covers the preparation and reactions of these compounds.[102]

I	II	III
a R=Ph	a R=R'=Ph	a R=R'=Ph
b R=p-CH₃Ph	b R=Ph, R'=Me	b R=Ph, R'=Me
	c R=R'=p-CH₃Ph	c R=R'=Me

43
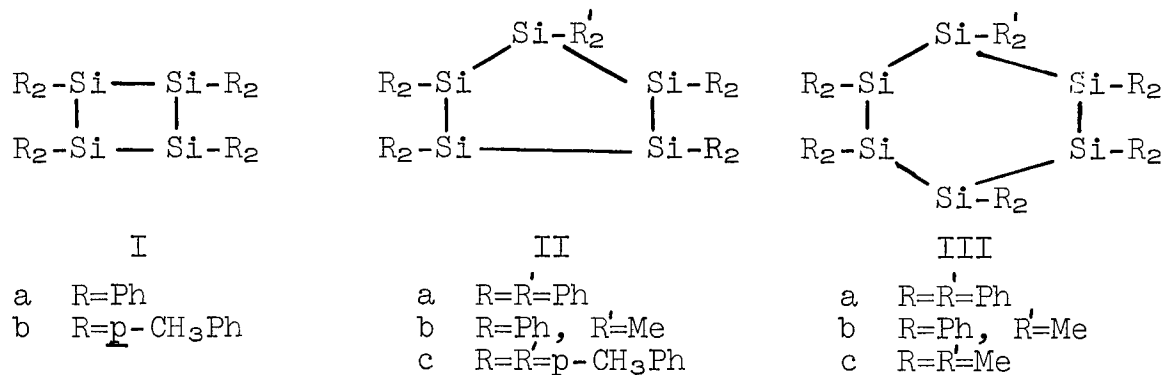
Only a few heterocyclic compounds containing the Si-Si bond have been prepared and little or no study has been made on the reactions of these compounds. Excluding compounds containing carbon in the ring, most of the known compounds contain oxygen as the hetero atom. Derivatives having structures IV-IX have been prepared.

R_2-Si, Si-R_2, O, Si——Si, R_2, R_2

R_2-Si, Si-R_2, O, R_2-Si, Si-R_2, Si, R_2

R_2-Si, Si-R_2, O, R_2-Si, Si-R_2, Si——Si, R_2, R_2

IV   V   VI

R=Ph   R=Ph   R=Me

R_2-Si, Si-R_2, O, R_2-Si, Si-R_2, O

R_2-Si, Si-R_2, O, O, Si-R_2, Si, R_2

R_2-Si, Si-R_2, O, O, O, Si——Si, R_2, R_2

VII   VIII   IX
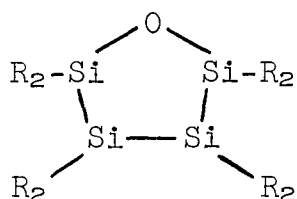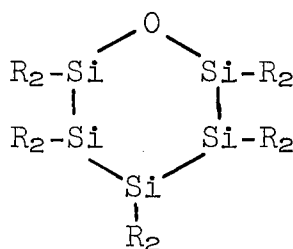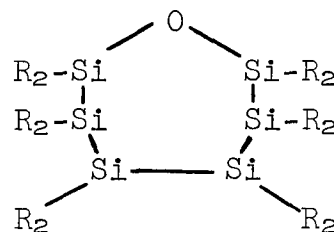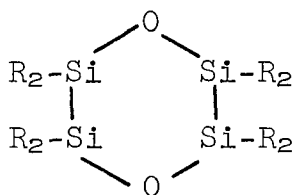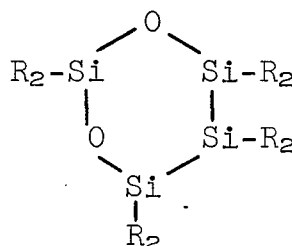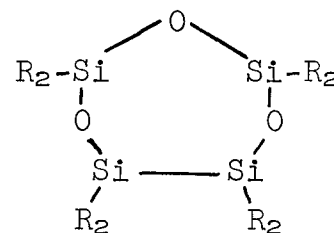
a   R=Ph   R=Ph   a   R=Ph
b   R=Me   b   R=Me

Kipping prepared IV by direct oxidation of Ia[97] and by hydrolysis of the dihalo derivatives of Ia. He also obtained two compounds having the general formula $Ph_8Si_4O_2$ for which he proposed structures VIIa and VIII.[97] One of these compounds, called the "rhomboidal oxide", was prepared by the oxidation of IV with nitric acid. The same compound was prepared by the dehydration of 1,1,2,2-tetraphenyldisilane-1,2-diol showing the compound to be VIIa.[105] The other isomer obtained by the reaction of nitrobenzene on Ia was assumed to be VIII.[105] Kumada has reported VIIb from the hydrolysis of 1,2-dihalo- and diethoxytetramethyldisilanes[17] and IXb from the co-hydrolysis of diethoxydimethylsilane and 1,2-diethoxy-tetramethyldisilane.[106] Compounds V and VI have been obtained only in very low yields by dehydration of the corresponding α, ω-diols.[107]

The present report describes the unambiguous synthesis of IV, VIIa, VIII, IXa and of octaphenylcyclotetrasiloxane, and we include a study of the reactions of these compounds with chlorine and nitrobenzene.

Starting with compound Ia, compounds IVa, VIIa, VIII, IXa and octaphenylcyclotetrasiloxane can be made in essentially quantitative yields by the insertion of one oxygen atom at a time into the ring using a procedure involving hydrolysis subsequent to chlorination of the appropriate smaller ring compound. Parallel to the above syntheses was the preparation and study of α,ω-dichloro-perphenylatedtetrasilanes containing one, two, three and four oxygen atoms in the polysilane chain.

The addition of chlorine to Ia in ether, pentane or petroleum ether (b.p. 60-70°C) provides a quantitative preparation of 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane.[108] The hydrolysis of the dichloride with hot propyl alcohol gave octaphenyloxatetrasilacyclopentane (IVa) quantitatively. Cyclization to the five-membered ring monoxide was so facile that attempts to prepare a 1,4-dipropoxy derivative by hydrolysis at lower temperatures resulted only in recovery of starting material and a lower yield of the cyclic oxide. This is quite different from 1,5-dichloro-1,1,2,2,3,3,4,4,5,5-decaphenylpentasilane which gave only the 1,5-dipropoxy derivative in good yield when treated with hot propyl alcohol.[108] Also the 1,6-dichloropolysilane (XIII) (see below) gave the dipropoxy derivative in high yield when treated with propyl alcohol at 30°C.

$$\text{Ia} \xrightarrow{\text{Cl}_2} \text{Cl-}(\text{SiPh}_2)_4\text{-Cl} \xrightarrow{\text{PrOH}} \begin{array}{c} \text{Ph}_2\text{-Si} \longrightarrow \text{Si-Ph}_2 \\ | \qquad\qquad | \\ \text{Ph}_2\text{-Si} \qquad \text{Si-Ph}_2 \\ \diagdown \qquad \diagup \\ \text{O} \end{array}$$

IV

$$\text{IIa} \xrightarrow{\text{Cl}_2} \text{Cl-}(\text{SiPh}_2)_5\text{-Cl} \xrightarrow{\text{PrOH}} \text{PrO-}(\text{SiPh}_2)_5\text{-OPr}$$
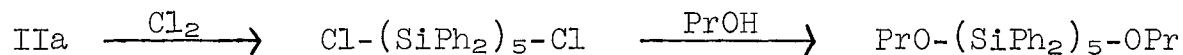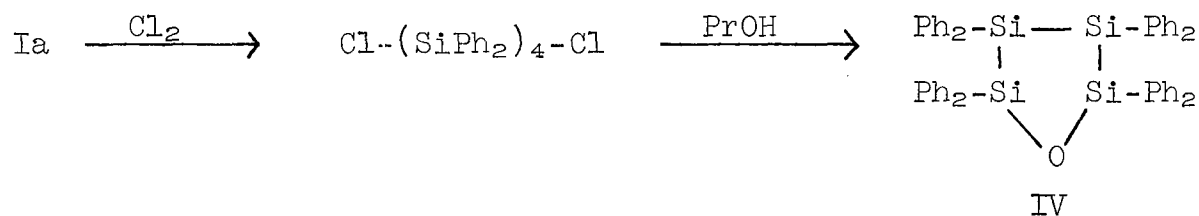
Octaphenyloxatetrasilacyclopentane (IV) reacts readily with chlorine in petroleum ether (b.p. 60-70°C) or with

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phosphorus pentachloride in refluxing 1,1,2,2-tetrachloro-
ethane or benzene to form two α,ω-dichlorooxatetrasila-
pentanes: 1-chloro-3(chlorodiphenylsiloxy)-1,1,2,2,3,3-
hexaphenyltrisilane (XII) and 1,3-bis(chlorodiphenylsilyl)-
1,1,3,3-tetraphenyldisiloxane (XI). The two isomeric pro-
ducts were difficult to separate by fractional recrystalli-
zation and only small quantities of each were obtained pure
for analysis. Identification was achieved by hydrolysis
of XI to the known[105] octaphenyl-1,4-dioxa-2,3,5,6-tetra-
silacyclohexane (VIIa).
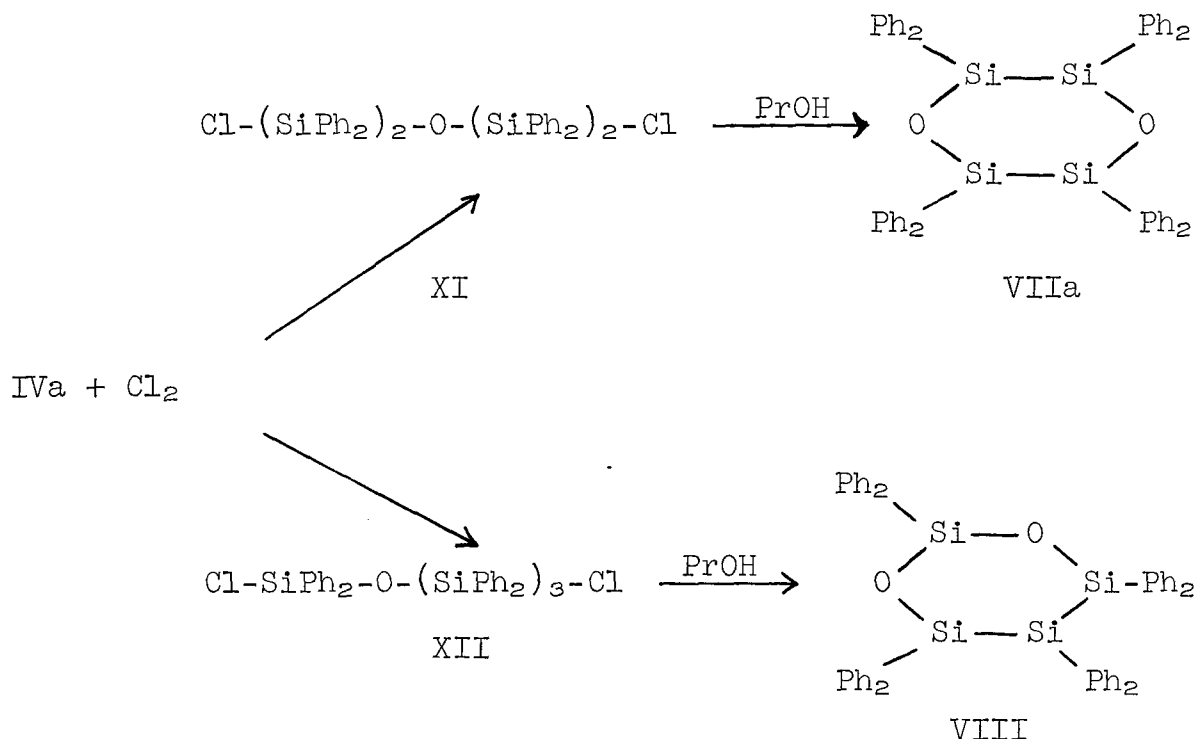
VIIa was found to be insoluble in hot acetone and
nearly insoluble in hot benzene while VIII was readily
soluble in hot acetone and cold benzene. It is inter-
esting to note that the symmetrical products in both
the chlorination and hydrolysis had the lower melting
points with XI melting at 114-116°C while XII melted
at 169-170°C, VIIa at 227-228°C and VIII at 256-257°C.

After isolation of the hydrolysis products it was
ascertained that the chlorination of the monoxide was
quantitative. The cleavage reaction rather than being

random, favored by a factor of 3:1, the cleavage of the silicon-silicon bond farthest from the oxygen atom. This is to be expected, as the electronegative oxygen atom would make adjacent silicon atoms less susceptible to oxidation.[109] Delocalization of unshared electron pairs from the oxygen atom to free d orbitals of the adjacent silicon atoms retarding possible formation of a pentacovalent intermediate would also be a factor contributing to the observed ratio.[109] Possibly due to ring conformation, these effects appear to be decreased in a heterocyclic polysilane. This can best be demonstrated by the rapid cleavage of IXa with chlorine as compared to no observed cleavage of the linear compounds, XI, XIII or XIV with chlorine under comparable conditions.

The reaction of IV with chlorine appears to be nearly as fast as the reaction of Ia with chlorine. Again, this is in contrast to the reactions of the five-membered ring, IIa, which reacts very slowly with chlorine in petroleum ether (b.p. 60-70°C) and not at all with equimolar quantities of phosphorous pentachloride in benzene.[108] Steric factors are believed to play an important part in the latter reaction.[102] However, this rapid decrease in reactivity, with increasing ring size, has also been noted in comparisons of nucleophilic cleavage of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane.[110] The decrease in reactivity, with increasing ring size, was attributed to be due to differences in ground and transition state energies caused by ring strain and steric factors in the formation of a pentacovalent intermediate. These same properties may in part account for the reactions observed in this report. This can best be demonstrated by a comparison of the effect of adding chlorine to IXa and XIV. The adjacent electronegative or electron donor properties of oxygen may decrease the ground state energy of XIV more than that of IXa due to conformational effects as well as ring strain. The same electron delocalization of the oxygen atom would cause a decrease in the transition energy of IXa as compared to that of XIV. This does not, however, account for the inability of chlorine to cleave compounds such as 1,4-dichlorooctaphenyltetrasilane under the conditions used. The addition of chlorine to a heterogeneous suspension of a solid in petroleum ether to give an insoluble product is in itself a somewhat unusual process. Solubility and solvent effects, difficult to interpret, are undoubtedly involved. Chlorine adds rapidly to dichloroperphenylated-linear and cyclic polysilanes in solution.[108] Evidence was shown that the mechanism may be through a free radical rather than a nucleophilic attack.

Compound VIII reacted rapidly with chlorine in petroleum ether (b.p. 60-70°C). Ring cleavage of the trisilane at either silicon-silicon bond provides the same product, 1-chloro-5-(chlorodiphenylsilyl)-1,1,3,3-5,5-hexaphenyltrisilane (XIII), and the yield was essentially quantitative. The product was easily hydrolyzed unless some care was taken to prevent exposure to moist air while recrystallizing.

Treatment of XIII with propyl alcohol at room temperature provided a high yield of a dipropoxy derivative, 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxy-trisiloxane (XVI) and a small amount of the cyclic trioxide, octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa). Repeating the reaction with refluxing propyl alcohol increased the yield of the cyclic trioxide (IXa) to 43-65% with only small amounts of XVI being isolated. However, the treatment of XVI with hot propyl alcohol resulted only in recovered XVI. A continuous slow addition of anhydrous hydrogen chloride to hot propyl alcohol containing XVI did cause cyclization and a 55% yield of IXa was obtained.

The pyrolysis of a small amount of XVI at 300°C left only a light straw colored viscous polymer. No evidence for the formation of IXa was found. The infrared spectrum of the resin was similar to the spectrum of XVI. Telomerzation appeared to occur rather than cyclization or decomposition.

Compound VIIa was found to be nearly as insoluble as Ia in most solvents and it resisted all attempts to cleave the silicon-silicon bonds with chlorine in petroleum ether (b.p. 60-70°C) or n-pentane. However, it was found that the reaction proceeded smoothly with a suspension of VIIa in a mixture of carbon tetrachloride and ether or carbon tetrachloride and petroleum ether (b.p. 60-70°C). The product,1,6-dichloro-1,1,3,3,4,4,6,6-octa-phenyl-2,5-dioxa-1,3,4,6-tetrasilahexane (XIV), which was obtained in high yield, was hydrolyzed in hot propyl alcohol to yield the same cyclic trioxide (IXa) as obtained by hydrolysis of XIII. The hydrolysis in hot propyl alcohol gave a mixture of IXa and the dipropoxy derivative, 5,5,7,7,8,8,10,10-octaphenyl-4,6,9,11-tetraoxa-5,7,8,10-tetrasilatetradecane (XVII). Continuous slow addition of anhydrous hydrogen chloride to hot propyl alcohol and then addition of XIV to the hot mixture gave IXa (79%) as the only isolable product.

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Ph₂
 \
  Si —— O
 /   \
O   Si-Ph₂   Cl₂
 \   /   ⟶   Cl-SiPh₂-O-SiPh₂-O-SiPh₂SiPh₂-Cl
  Si —— Si   XIII
 /   \
Ph₂   Ph₂

VIIIa

PrOH ↙   HCl │ PrOH

PrO-SiPh₂-O-SiPh₂-O-SiPh₂SiPh₂-OPr

XVI

                                    HCl
                                   ⟶   Ph₂Si   Si-Ph₂
                                   PrOH   \   O   /
                                                  O   O
PrO-SiPh₂-O-SiPh₂SiPh₂-O-SiPh₂-OPr   \   /
                                                   Si — Si
XVII   /   \
                                                Ph₂   Ph₂
                                                       IXa

       PrOH ↖   HCl   ↗ PrOH

Ph₂-Si —— Si-Ph₂
   /   \
  O   O   Cl₂
   \   /   ⟶   Cl-SiPh₂-O-SiPh₂SiPh₂-O-SiPh₂-Cl
Ph₂-Si —— Si-Ph₂   XIV

VIIa
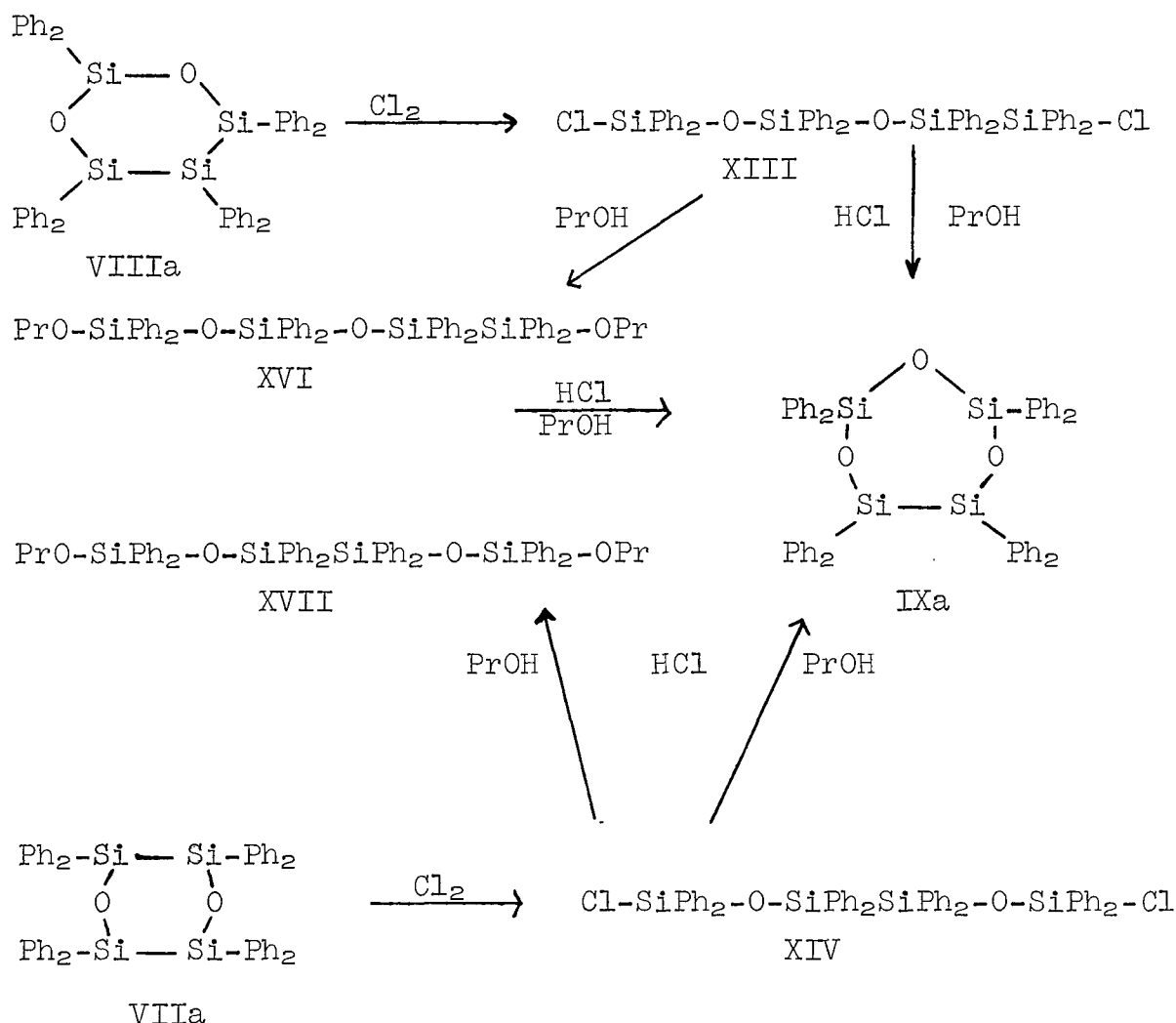
IXa, which was also prepared by the reaction of nitro-
benzene on Ia and on IV (see below), gave constant melting
fractions at 221-222°C, 231-232°C and at intermediate ranges.
The X-ray powder pattern photographs of IXa, obtained from
the hydrolysis of XIII, m.p. 231-232°C, and from the re-
action of nitrobenzene on IV, m.p. 221-222°C, were not
identical indicating that the compound existed in at least
two isomorphic forms. No spectral, analytical or chemical
evidence was found to indicate they were not the same com-
pound.

       The crude product obtained from the cleavage of IXa
in a carbon tetrachloride-petroleum ether (b.p. 60-70°C)
mixture was identified as 1,7-dichloro-1,1,3,3,5,5,7,7-
octaphenyltetrasiloxane. The 84% yield was slightly less

than that of the smaller ring homologs. None of the
starting material was recovered. The hydrolysis of the
dichloro derivative occurred readily during recrystalli-
zation and only small fractions of the compound were iso-
lated pure. It was found, surprisingly, in contrast to
VIIa, that IXa reacted readily with chlorine in petroleum
ether (b.p. 60-70°C) to provide XVIII in good yield.

$$Ph_2-Si \underset{\underset{O}{|}}{} \quad Si-Ph_2 \underset{\underset{O}{|}}{} \qquad \xrightarrow{Cl_2} \qquad Cl-SiPh_2-(OSiPh_2)_3-Cl$$

IXa

XVIII

$$XVIII \qquad \xrightarrow[HCl]{PrOH} \qquad XIX$$
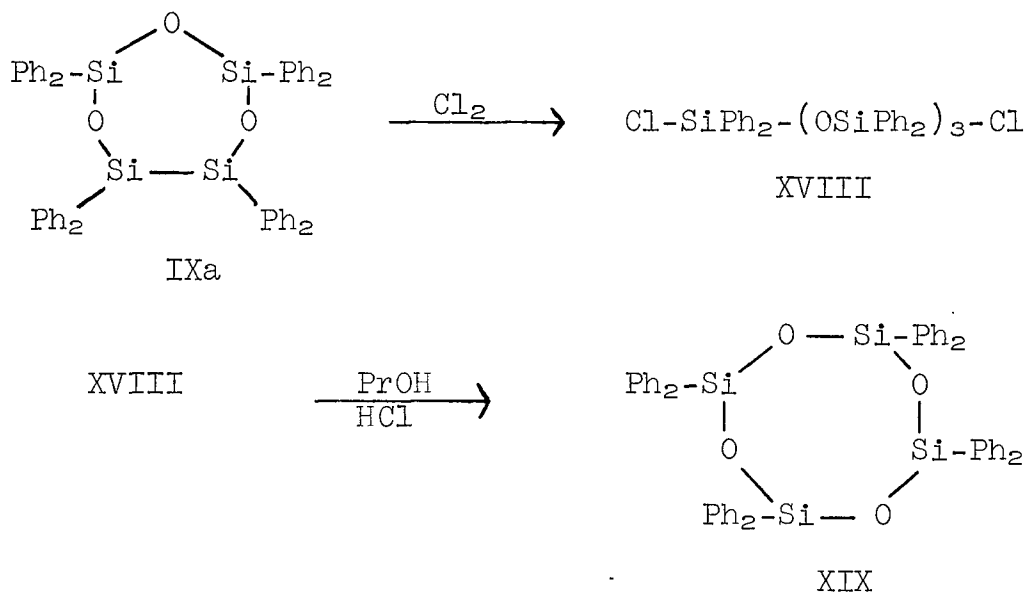
All of the cyclosilanes investigated reacted readily
with chlorine in petroleum ether (b.p. 60-70°C) regard-
less of ring size, with the exception of VIIa. No evi-
dence was found for any silicon-silicon bond cleavage of
any straight chain polysilane under the conditions specified.

Attempts to prepare XIX by the treatment of XVIII
with hot propyl alcohol gave only mixtures from which no
pure fractions were obtained. As an additional proof of
structure of IXa, XVIII was prepared by chlorination of
IXa obtained from the hydrolysis of XIII and of XIV. This
sample was hydrolyzed in hot propyl alcohol continuously
saturated with anhydrous hydrogen chloride. An 82% yield
of XIX was obtained. Although attempts to prepare and
isolate XVIII and to hydrolyze it to XIX have been made,[111]
this is the first reported successful unambiguous syn-
thesis of XVIII and of XIX.

A discrepancy of 11°C in the melting point was found
in compound VIII and the compound believed to have the
same structure[105] prepared by Kipping from the reaction of

nitrobenzene and Ia.[97] The reaction was repeated in the manner described by Kipping using a much larger quantity of starting material than was available to Kipping. Our studies were extended to include the reaction of nitrobenzene on IV, VIIa, VIII, IIIa, IIa and hexaphenyldisilane.

Below 140°C very little reaction occurred between nitrobenzene and Ia. However, at 165°C the reaction became rapidly exothermic and was complete in a few minutes. The products obtained consisted of unidentified black tars and approximately 50%, based on starting material, of crystalline solids. Recrystallization to a constant melting point yielded a product presumably the same as that reported by Kipping, m.p. 245-246°C.[97]

An infrared spectrum of the compound showed an Si-O-Si bond absorption at 9.77 μ and a shoulder at 9.43 μ. After repeated recrystallizations the melting point of the major fraction remained constant, but small fractions melted at 255-257°C and gave Si-O-Si absorptions in the infrared region only at 9.81 μ (see Table I). Also obtained were fractions melting at 219-220°C and 231-232°C. These last fractions gave only strong Si-O-Si absorptions in the infrared region at 9.44 μ identical to that of IXa. It appears that Kipping's compound may well have been an eutectic mixture of VIII and IXa.

X-ray powder pattern photographs of a fraction having a constant m.p. 245-246°C and of VIII, m.p. 256-257°C, obtained from the hydrolysis of XII, were identical. This would indicate the two compounds were identical and not different isomorphic forms of the same compound. The quantity of IXa in the eutectic is evidently too small to be observed in the X-ray pattern photograph. An infrared spectrum of a mixture of VIII and IXa gave an identical spectrum to that of the eutectic.

Infrared studies of lower melting trace fractions from the reaction of Ia and nitrobenzene indicated the presence of XIX and of hexaphenylcyclotrisiloxane.

No evidence for the presence of IV was found from the reaction of Ia and nitrobenzene. However, it was found that IV reacted only slowly with hot nitrobenzene. The major crystalline product was IXa. With incomplete reaction of IV, small fractions of VIII were found to be present.

As was observed by Kipping[97] very little reaction was found to occur with VIIa and VIII on short contact with refluxing nitrobenzene. However, treatment with refluxing nitrobenzene for longer periods caused complete reaction with unidentified black tars again the major product. A 40-42% yield, based on starting material, of crystalline solid was obtained from VIIa and VIII. From this solid was isolated XIX, hexaphenyltrisiloxane and eutectic mixtures of these two compounds.

The isomorphic forms and eutectic mixtures of these two compounds have been well characterized.[111-113] Our investigations indicate that VIII and IXa exhibit similar properties. No VIIa was isolated as a product from any of the reactions with nitrobenzene. Compound VIIa was the only heterocyclic compound prepared which showed no isomorphic properties. As a result of its insolubility it was easily separated from VIII, the only other compound in reaction mixtures containing VIIa.

Ultraviolet and infrared spectra were particularly useful in the identification and characterization of the compounds. Characteristic infrared absorptions due to Si-O-Si groups have been found to shift significantly with increasing ring size. The five-membered ring IV gives a characteristic band at 10.45μ.[105] Characteristic cyclotrisiloxane bands are shifted to 9.8μ while cyclic tetramers and pentamers have a band at 9.2μ which gradually widens and splits with larger rings.[114,91] The seven-membered ring, IXa, gave absorptions at 9.45μ.

Table I lists the Si-O-Si bond infrared absorptions found in several linear and cyclic siloxane compounds. Comparison of the six-membered rings, VIIa and VIII (9.81μ) with hexaphenylcyclotrisiloxane (9.88μ) which is planar[115] would indicate a similar ring strain and one might expect a planar structure for these compounds. The absorption of IXa at 9.45μ is identical to that of the straight chain α, ω-dichloro compounds and the bonding would appear to be strain-free. The cyclotetrasiloxane is a non-planar structure.[116]

The characteristic Si-phenyl absorption at 8.9μ has been observed to split when two phenyls are present on the same atom but revert to a single absorption for the triphenylsilyl group.[91] In our studies it was observed

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that a diphenylsilylene group splits to give a doublet at 8.87 and 8.97 μ. A tetraphenyldisilanylene[+] group gave a single absorption at 9.06 μ or a poorly resolved doublet at 9.02 and 9.06 μ. A hexaphenyltrisilanylene[+] group gives a single absorption at 9.07 μ. Consequently a compound having a mono- and a trisilane moiety gave a triplet at 8.92, 9.00 and 9.06 μ and a compound with a mono- and a disilane moiety gave a doublet at 8.92 and 9.05 μ. Characteristic absorptions found are listed in Table I for the respective compounds.

Recent studies on ultraviolet absorptions of polysilanes[77,117-120] have given ample evidence for the utility of this method for characterization and identification of polysilanes. Table II lists the ultraviolet spectra λ_{max} values for the compounds prepared and λ_{max} for similar polysilanes.

B. Experimental

All reactions were carried out in oven-dried glassware under atmospheres of oxygen-free, dry nitrogen. All hydrocarbon solvents were stored over sodium wire. Other reagents and gases were used as they were obtained commercially. The reaction apparatus consisted of a standard taper flask equipped with a stirrer, thermometer, condenser and, as required, a gas inlet tube which extended below the liquid level. A trap having the same volume as the reaction vessel was placed between it and the gas source. The chlorine was metered by passing it through a 1 mm. capillary 3 cm. long. The pressure drop across this orifice was measured with a manometer filled with carbon tetrachloride. The calibration was based on the water displacement of air in an inverted 500 ml. graduate. Temperatures are uncorrected and melting points were obtained with a Mel-Temp apparatus. Spectra were determined using a Perkin Elmer Model 21 Spectrophotometer and a Beckman-DK-2A Spectrophotometer. Letters indicate the relative intensity of absorption bands: s = strong, m = medium, w = weak, sh = shoulder. Molecular weight determinations were made with a Mechrolab Model 301-A Vapor Pressure Osmometer. Benzil was used as a standard with benzene as solvent with the exception of one case in which acetone was used with comparable results.

[+] Silicon radical nomenclature is discussed by C. Eaborn, Organosilicon Compounds, Butterworths Scientific Publications, London, 1st ed., 1960, p. 3.

TABLE XX

Si-phenyl and Si-O-Si Bond Infrared Absorptions
in the 8.5-11.0 μ Region

Compound	Characteristic band position (μ) (in CS_2)	
	Si-phenyl	Si-O-Si[a]
$(Ph_2SiO)_3$	8.88, 8.97	9.87
$(Ph_2SiO)_4$	8.88, 8.96 (small)	9.25
Ph_8Si_4O (IV)	9.08	10.45[105]
$Ph_{10}Si_5O$ (V)	9.08	9.80[107]
$Ph_8Si_4O_2$ (VIIa)	9.02, 9.07 (small)	9.84
$Ph_8Si_4O_2$ (VIII)	8.90, 8.97, 9.07	9.81
$Ph_8Si_4O_3$ (IXa)	8.90, 8.97[b]	9.44
$Me_{12}Si_6O$ (VI)		9.60[107]
$Cl-SiPh_2-O-(SiPh_2)_3-Cl$	8.92, 9.0, 9.07	9.50
$Cl-(SiPh_2)_2-O-(SiPh_2)_2-Cl$	9.06	9.47
$Cl-(SiPh_2)_2-(OSiPh_2)_2-Cl$	8.92, 9.07	9.50
$(Cl-SiPh_2-O-SiPh_2)_2$	8.92, 8.97[b]	9.47
$Cl-SiPh_2-(OSiPh_2)_3-Cl$	8.90	9.50

[a]All of the Si-O-Si absorptions were broad except in the
six-membered rings. [b]These samples showed weak shoulders
at 9.06 μ.

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TABLE XXI

U.V. Spectral Data of Some Polysilane and Siloxanes

Compound	Band Position, (cyclohexane) λ max. mμ.
$(Ph_2SiO)_4$	253, 259, 264.5, 270.5
Ph_8Si_4O (IV)	253
$Ph_{10}Si_5O$ (V)	250 (sh)[108]
$Ph_8Si_4O_2$ (VIIa)	245
$Ph_8Si_4O_2$ (VIII)	256
$Ph_8Si_4O_3$ (IXa)	239 (sh)
$Me_{12}Si_6$ (IIIc)	232, 255 (sh)[120]
$Me_{12}Si_6O$ (VI)	239[108]
$(SiPh_2)_4$ (Ia)	234, 270[120]
$(SiPh_2)_5$ (IIa)	251 (sh)[120]
$Me_2Ph_8Si_4$ (IIb)	249 (sh)[120]
$(SiPh_2)_6$ (IIIa)	248 (sh)[120]
$Cl-SiPh_2-O-(SiPh_2)_3-Cl$	245 (sh)
$Cl-(SiPh_2)_2-O-(SiPh_2)_2-Cl$	240 (sh)
$Cl-(SiPh_2)_2-(OSiPh_2)_2-Cl$	240.5 (sh)
$(Cl-SiPh_2-O-SiPh_2)_2$	----[a]
$Cl-SiPh_2-(OSiPh_2)_3-Cl$	254, 259, 264.5, 271
$PrO-(SiPh_2)_2-(OSiPh_2)_2-OPr$	245 (sh)
$(PrO-SiPh_2-O-SiPh_2)_2$	243
$PrO-SiPh_2-(OSiPh_2)_3-OPr$	252, 258, 263, 270
$PrO-SiPh_2SiPh_2-OPr$	243[108]
$H-SiPh_2SiPh_2-H$	234[104]
$Me-SiPh_2SiPh_2-Me$	239[77]
$Ph-SiPh_2SiPh_2-Ph$	246.5[121]
$H(SiPh_2)_3H$	249.5[122]
$Cl-(SiPh_2)_3-Cl$	245 (w sh)[108]
$Ph-(SiPh_2)_3-Ph$	254[120]

[a]A shoulder too weak to estimate was observed.

Preparation of 1,4-dichlorooctaphenyltetrasilane. Chlorine
gas was added at approximately 200 ml./min. (3 l., 0.12 mole)
to a suspension of octaphenylcyclotetrasilane, 21.9 gm.
(0.03 mole), in 150 ml. of petroleum ether (b.p. 60-70°C).
The temperature was maintained at 15-25°C with an ice-bath.
The excess of chlorine was removed under reduced pressure
and the solids were filtered off to provide 24.0 gm. (100%)
of 1,4-dichlorooctaphenyltetrasilane, m.p. and mixture m.p.
with an authentic sample 186-187°C.[97,108]

Preparation of octaphenyloxatetrasilacyclopentane. 1,4-
Dichlorooctaphenyltetrasilane, 24.0 gm. (0.03 mole), was
heated at reflux in 150 ml. of propyl alcohol for 4 hours.
The reaction mixture was then cooled and filtered to
give 22.1 gm. (99%) of octaphenyloxatetrasilacyclopentane.
Recrystallization and infrared spectra comparisons indi-
cated that the compound was pure but it was found that
the melting point varied as reported earlier.[+] As with
VIII (see below), the melting point was dependent upon
the temperature at which the sample was placed in the
melting point block. However, with IV it was observed
that introduction of a fresh sample at temperatures be-
tween 240-270°C caused sintering and gave melting points
approximately 6°C above the temperature at which the
sample was introduced. A sharp distinct melting point
was obtained at 282-283°C with addition of the sample
to the block at 280°C at a temperature increase of 1.5°C/min.
The ultraviolet absorption in cyclohexane gave a λ_{max}., 253
mμ (sh). The infrared spectrum (in CS_2) showed the following
absorptions in μ : 3.27 (m), 5.13, 5.31, 5.52, 7.30, 7.52,
7.72, 7.95 (w), 8.42 (m), 9.08 (s), 9.42 (w), 9.75, 10.03
(m), 10.45, 13.64, 14.44 (s), and 15.05 (m). The strong
absorption of the silicon-oxygen bond at 10.45 μ is
characteristic of this cyclic oxide and provided identi-
fication.[105]

Preparation of 1,4-dipropoxyoctaphenyltetrasilane. (Attempted).
Eight grams (0.01 mole) of 1,4-dichlorooctaphenyltetra-
silane, m.p. 186-187°C, was stirred in 100 ml. of propyl
alcohol at 37°C for 7 hours. After filtration, 7.9 gm.
(99%) of solid melting at 179-181°C was obtained. Ex-
traction with 100 ml. of hot petroleum ether (b.p. 80-
115°C) left 1.0 gm. of insoluble material, m.p. 206-222°C.
The infrared spectrum of this latter fraction indicated

[+]Kipping reported[97]: "The melting of such preparations were
  most indefinite and irregular; some samples sintered from
  205-210°C and melted complete at about 220°C; others did
  not sinter until about 220°C and melted gradually up to
  245°C or occasionally as high at 250-260°C."

the presence of octaphenyloxatetrasilacyclopentane (see above). No absorption was noted in the region of aliphatic CH stretching vibrations as evidenced by other silylpropoxy compounds (see below).

Octaphenyloxatetrasilacyclopentane and phosphorous pentachloride.

     a. <u>In tetrachloroethane</u>. A mixture containing 75 ml. of tetrachloroethane, 7.45 gm. (0.01 mole) of octaphenyloxa-tetrasilacyclopentane and 2.1 gm. (0.01 mole) of phos-phorus pentachloride was heated at 140°C for 10 min. The reaction mixture was then cooled and the solvent re-moved by distillation under reduced pressure. The residue was dissolved in benzene and 50 ml. of petroleum ether (b.p. 60-70°C) added. Upon standing overnight 1.8 gm. (22%) of solid, m.p. 162-163°C, was obtained. Repeated recrystallizations provided 0.9 gm. (11%) of a pure com-pound, m.p. 169-170°C, identified by its hydrolysis pro-duct as 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII) (see below). The ultraviolet spectrum in cyclohexane gave a λ_{max}., 245 mμ (sh). The infrared spectrum (in CS_2) showed absorptions in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.31, 7.51, 7.70, 7.95 (w), 8.42 (m), 8.67 (w), 8.92, 9.01, 9.07 (s triplet), 9.50 (s), 9.76, 10.04 (m), 13.64, 13.97, 14.45 (s).

     <u>Anal</u>. Calcd. for $C_{48}H_{40}Cl_2OSi_4$: Si, 13.76; mol. wt., 816; Found: Si, 13.68, 13.61; mol. wt., 807.

     b. <u>In benzene</u>. Octaphenyloxatetrasilacyclopentane, 14.9 gm. (0.02 mole), phosphorus pentachloride, 4.5 gm. (0.022 mole), and 100 ml. of benzene were heated at 81°C for 10 min. The reaction was then cooled and the solvent removed by distillation under reduced pressure. Recrystalli-zation of the residue from benzene-petroleum ether (b.p. 60-70°C) provided 13.3 gm. (81.5%) of solid, m.p. 125-182°C. Repeated fractional recrystallizations gave two pure compounds: 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltri-silane (XII), 1.5 gm. (9%), m.p. and mixture m.p. with an authentic sample (see above) 169-170°C and 1,3-bis(chloro-diphenylsilyl)-1,1,3,3-tetraphenyldisiloxane (XI), 1.3 gm. (8%), m.p. 114-116°C, identified by its hydrolysis product (see below). The latter compound gave an ultraviolet spectrum maximum as a weak shoulder at 240 mμ in cyclohexane. The infrared spectrum contained absorptions (in CS_2) in μ at: 3.27 (m), 5.13, 5.30, 7.31, 7.51, 7.70, 7.94 (w), 8.42 (m), 8.68 (w), 9.06, 9.47 (s), 9.78, 10.04 (m), 13.59 (s), 14.27 (sh), 14.40 (s).

Anal. Calcd. for $C_{48}H_{40}Cl_2OSi_4$: Si, 13.76; mol. wt., 816. Found: Si, 13.77, 13.67; mol. wt., 803, 796.

Octaphenyloxatetrasilacyclopentane and chlorine. Chlorine was added at approximately 200 ml./min. to a suspension of 22.4 gm. (0.03 mole) of octaphenyloxatetrasilacyclopentane in 150 ml. of petroleum ether (b.p. 60-70°C) for 10 min. (2 l; 0.082 mole) between 10-20°C. The excess of chlorine and part of the solvent were removed under reduced pressure. The solid was then filtered off and 21.1 gm. (86%) of crystalline material was obtained, melting over the range 140-145°C. The solvent was concentrated to give an additional 2.6 gm. (11%), m.p. 127-128°C. The overall yield of solid was 97%. The reaction was repeated several times with the yield of the mixture of products being between 94-98% (based on a 1:1 molar ratio addition of chlorine). A 40 gm. mixture, m.p. 137-163°C, of the reaction products was fractionally crystallized in benzene-petroleum ether (b.p. 60-70°C) mixtures. A 3.55 gm. (9%) sample of 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane, m.p. 169-170°C, was the only pure product isolated. The separation of the hydrolysis products showed that the reaction was nearly quantitative and that there were only two products, 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane and 1,3-bis(chlorodiphenylsiloxy)-1,1,3,3-tetraphenyldisiloxane (see below).

Propyl alcohol hydrolysis of 1-chloro-3-(chlorodiphenylsiloxy)-1,1,2,2,3,3-hexaphenyltrisilane (XII). Three gm. (0.0037 mole) of XII was heated at reflux temperature in 80 ml. of propyl alcohol for 16 hours. Upon cooling, 2.4 gm. (86%) of solid melting at 246-249°C was obtained. Concentration of the filtrate provided only trace amounts of solid. The product was then recrystallized in a benzene-petroleum ether (b.p. 60-70°C) mixture to provide 0.8 gm. (29.6%) of a pure compound, m.p. 257-257.5°C. If a sample of the compound was placed in the melting point block at temperatures lower than 250°C the melting point was lowered e.g. a sample introduced at 150°C melted at 242-244°C and another introduced at 240°C melted at 254-255°C. The maximum melting point obtained was 257-257.5°C. A mixture m.p. with a compound prepared from the reaction of octaphenylcyclotetrasilane and nitrobenzene, as described by Kipping,[97] m.p. 245-246°C, and tentatively identified[105] as octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane, (VIII) melted mid-way between the two. X-ray powder pattern photographs of the two compounds indicated they were identical. Repeated recrystallizations in petroleum ether (b.p. 80-115°C) of the product

obtained from nitrobenzene and (Ia) gave fractions that had a m.p. and mixture m.p. of 255-257°C (see below). The ultraviolet absorption spectrum in cyclohexane showed λmax., 256 mμ. The infrared spectrum gave absorptions (in CS_2) in μ at: 3.25 (m), 5.12, 5.30, 5.50, 6.1, 7.3, 7.55, 7.72, 7.94 (w), 8.43 (m), 8.92, 8.99, 9.07 (s triplet), 9.65, 9.80, 9.97 (s), 10.07 (m), 13.63, 14.00, 14.40 (s), 14.83 (m).

Anal. Calcd. for $C_{48}H_{40}O_2Si_4$: Si, 14.76; mol. wt., 761; hydrogen value[123], 58.8 ml./gm. Found: Si, 14.64, 14.71; mol. wt., 746, 745, 748; hydrogen value, 54.1 ml./gm.

Preparation of octaphenyl-1,3- and 1,4-dioxaoctaphenyl-tetrasilacyclohexane. Octaphenyloxatetrasilacyclopentane, 22.0 gm. (0.0296 mole), was added to 180 ml. of petroleum ether (b.p. 60-70°C). Chlorine was added to the suspension at 200 ml/min. for 25 min. (5 1; 0.2 mole) between 15-25°C. The temperature was held at 25°C with an ice-bath. The excess chlorine was removed and the solid filtered off to give 23.0 gm. (95.5%) of crystalline material, m.p. 134-146°C. This material (0.0282 mole) was then added to 180 ml. of propyl alcohol and the mixture was refluxed for 20 hours. Upon filtering, cooling and con-centration of the solvent two fractions of crystalline material were obtained, 16.7 gm. (78%), melting over the range 227-236°C and 4.1 gm. (19%) m.p. 253-256°C. Sepa-ration of the two cyclic oxides was easily affected by boiling the crude fractions in acetone. This procedure gave 12.5 gm. (58.5%) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VIIa), insoluble in hot acetone, m.p. 225-227°C, and 8.15 gm. (38%) of octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane, (VIII), m.p. and mixture m.p. with the previously prepared compound 255-256°C. In three reactions the percent of 1,4- and 1,3-dioxa derivatives was 54 and 40, 54 and 42 and 62 and 36%, respectively, with overall yields ranging from 94-98%. The 1,4-dioxa compound was identified by mixture m.p. with an uathentic sample prepared by the hydrolysis of 1,2-dibromotetraphenyldisilane.[108] Since a mixture m.p. depression is not observed by some similar silanes[+] the following additional properties are given. The ultra-violet absorption spectrum in cyclohexane gave a λ max.

[+]1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 161-162°C, 1-bromo-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 160-162°C, and 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane, m.p. 162-164°C, show no depression in a mixture m.p. with each other.

as a shoulder at 245 mμ. The infrared spectrum gave
absorptions (in CS_2) in μ at: 3.27 (m), 5.13, 5.30, 5.50,
7.0, 7.31, 7.6, 7.72, 7.94 (w), 8.42 (m), 9.01, 9.06 (s
doublet), 9.67, 9.81 (s), 10.05 (m), 13.57 (s), 14.24 (sh),
14.36 (s).

Anal. Calcd. for $C_{48}H_{40}O_2Si_4$: mol. wt., 761;
hydrogen value,[123] 58.8 ml./gm. Found: mol. wt., 741;
hydrogen value, 60.4.

Preparation of 1-chloro-5-(chlorodiphenylsilyl)-1,1,3,3-
5,5-hexaphenyltrisiloxane. Chlorine was added at 200 ml./min.
for 25 min. (5 l; 0.02 mole) to a suspension of 13.0 gm.
(0.017 mole) of octaphenyl-1,3-dioxa-2,4,5,6-tetrasila-
cyclohexane in 170 ml. of petroleum ether (b.p. 60-70°C).
The temperature was maintained between 18-32°C by means
of an ice-bath. The bright yellow color imparted to the
suspension by the chlorine rapidly disappeared at 32°C.
The excess of chlorine was removed under reduced pressure
and the solid was removed by filtration to give 12.0 gm.
(85%) of 1-chloro-5-(chlorodiphenylsilyl)-1,1,3,3,5,5-
hexaphenyltrisiloxane (XIII), m.p. 106-107°C. Recrystalli-
zation from petroleum ether (b.p. 60-70°C) caused no change
in the melting point. Concentration of the filtrate
provided an additional 1.3 gm. (9%), m.p. 103-106°C, and
0.3 gm. (2%) of crude product, m.p. 100-102°C. The ultra-
violet spectrum of the pure compound gave a λ max., 240.5
mμ (sh) in cyclohexane. The infrared spectrum (in CS_2)
gave the following absorptions in μ: 3.27 (m), 5.13,
5.31, 5.50, 7.31, 7.52, 7.70, 7.95 (w), 8.47 (m), 8.92
(s), 9.07 (sh), 9.49 (s), 9.75, 10.05 (m), 13.58, 13.95,
14.43 (s), 14.90 (m).

Anal. Calcd. for $C_{48}H_{40}Cl_2O_2Si_4$: Si, 13.63; mol.
wt., 832. Found: Si, 13.63, 13.65; mol. wt., 813.5, 801.

Preparation of 1,6-dichloro-1,1,3,3,4,4,6,6-octaphenyl-2,5-
dioxa-1,3,4,6-tetrasilahexane.

a. In petroleum ether. A suspension of 3.8 gm. (0.005
mole) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane
in 100 ml. of petroleum ether (b.p. 60-70°C) was treated
with chlorine gas added at 190 ml./min. for a period of
32 min. (6.1 l; 0.25 mole). The temperature rose from
28 to 35°C during the first 10 min., rose to 50°C in the
next 5 min. and was held at 53°C with an ice-bath. The
bright yellow color imparted by the chlorine rapidly dis-
appeared above 40°C. Removal of the solids by filtration
gave an 89.5% (3.4 gm.) recovery of the starting material,
m.p. 227-228°C. Distillation of the filtrate under re-

duced pressure provided 15.2 gm. of liquid having a boiling point above that of the solvent. A gas-liquid chromatographic analysis of the petroleum ether showed it contained 4 major components. A similar chromatogram of the high boiling liquid obtained above indicated the presence of 8 major components. The residue from the distillation was dissolved in 10 ml. of petroleum ether (b.p. 60-70°C) and after standing several hours 0.3 gm. (8%) of a crystalline white solid precipitated, m.p. 149-151°C.

b. In n-pentane. Chlorine gas was added at 200 ml./min. for 30 min. (6 1; 0.25 mole) to a suspension containing 7.6 gm. (0.01 mole) of octaphenyl-1,4-dioxa-2,3,5,6-tetra-silacyclohexane in 100 ml. of n-pentane. The temperature was maintained between 17-30°C with an ice-bath. Filtration of the reaction mixture gave a 7.45 gm. (98%) recovery of the starting material. A gas-liquid chromatogram indicated the filtrate contained two major components with a greater retention time than that of n-pentane. A treatment of n-pentane with chlorine under comparable conditions with comparisons by gas-liquid chromatography showed the solvent was chlorinated at about the same rate with or without the cyclosilane being present.

c. In carbon tetrachloride and petroleum ether. Octa-phenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane, 7.6 gm. (0.01 mole), suspended in 80 ml. of carbon tetrachloride and 50 ml. of petroleum ether (b.p. 60-70°C) was treated with chlorine at 200 ml./min. for 25 min. (5 1; 0.2 mole) between 16-34°C. Excess chlorine was removed under reduced pressure and 3.4 gm. of solid (41%), m.p. 149-151°C was obtained by filtration. Concentration of the solvents to 20 ml. and addition of 30 ml. of petroleum ether (b.p. 60-70°C) gave an additional 4.15 gm. (51%) of crystalline material, m.p. 148-150°C. Recrystallization gave a constant melting point of 149-150°C. The ultraviolet spectrum in cyclohexane gave a $\lambda_{max.}$, 244 mμ (sh). The infrared spectrum (in CS_2) gave the following absorptions in μ : 3.27 (m), 5.13, 5.30, 5.50, 7.30, 7.54, 7.70, 7.95 (w), 8.43 (m), 8.92, 9.00, 9.07 (s triplet), 9.47 (s), 9.76, 10.03 (m), 13.59, 13.95, 14.20 (sh), 14.39 (s), 14.89 (w).

Anal. Calcd. for $C_{48}H_{40}Cl_2O_2Si_4$: Si, 13.50; mol. wt., 832. Found: Si, 13.57, 13.53; mol. wt., 817, 823.

Propyl alcohol hydrolysis of 1-chloro-5-(chlorodiphenyl-
silyl)-1,1,3,3,5,5-hexaphenyltrisiloxane (XIII).

a. At 30-40°C. Propyl alcohol, 50 ml., was added to
10.8 gm. (0.013 mole) of (XIII) and the resulting sus-
pension was allowed to stand for 2 hours at 30-40°C and
then filtered. The solid obtained, 10.1 gm. (89%), m.p.
77-80°C was recrystallized from propyl alcohol to a con-
stant melting point, 79-80°C. Concentration of the
filtrate gave an additional 0.8 gm. (8%) of solid, m.p.
182-190°C. Recrystallization from petroleum ether (b.p.
80-115°C) provided 0.5 gm. (5%) of a pure compound, m.p.
223-226°C, identified in a later experiment as octaphenyl-
1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane. The low
melting material, m.p. 79-80°C, believed to be 1-(diphenyl-
propoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane
gave a $\lambda_{max.}$, 245 mμ (sh), in an ultraviolet spectrum in
cyclohexane. The infrared spectrum (in CS_2) contained
absorptions in μ at: 3.27, 3.38, 3.44, 3.50 (m), 5.12,
5.30, 5.49, 7.20, 7.28, 7.53, 7.68, 7.94 (w), 8.44 (m),
8.95, 9.07 (s), 9.24-9.54 (s broad), 9.75 (m), 9.86 (sh),
10.03 (m), 12.15 (m), 13.60, 13.97, 14.36 (s), 14.72 (w).

Anal. Calcd. for $C_{54}H_{54}O_4Si_4$: Si, 12.77; mol. wt.,
879. Found: Si, 12.95, 12.92; mol. wt., 895, 900.

b. At 98°C. Compound XIII, 4.1 gm. (0.005 mole), was
heated at reflux in 100 ml. of propyl alcohol for 3-4
hours. The suspension was allowed to stand several hours
and then filtered to yield 2.5 gm. (65.5%) of crystalline
solids, m.p. 226-228°C. Concentration of the filtrate
gave an additional 0.1 gm. (1.5%), m.p. 218-221°C. Re-
peated recrystallizations from petroleum ether (b.p.
80-115°C) gave a variety of fractions melting at 220-221°C,
231-232°C or at temperatures intermediate between these
limits. The first fractions from a recrystallization always
melted at 230-231°C with subsequent fractions at lower
melting points. It was determined by analysis, ultra-
violet, infrared, X-ray powder pattern photograph and
chemical reaction that the compound existed in at least
two isomorphic forms, one melting at 221-222°C and the
other at 231-232°C with mixtures of the two melting at
intermediate ranges. The ultraviolet spectrum in cyclo-
hexane gave a $\lambda_{max.}$, 239.5 mμ. The infrared spectrum
(in CS_2) gave the following absorption in μ: 3.27 (m),
5.13, 5.30, 5.50, 7.30, 7.55 7.72, 7.95 (w), 8.43 (m),
8.9, 8.97, 9.06 (s triplet), 9.47 (s), 9.76 (s), 10.04 (m),
13.59, 13.96, 14.38 (s), 14.80 (w), 15.47 (m).

Anal. Calcd. for $C_{48}H_{40}O_3Si_4$: Si, 14.44; mol. wt.,
777. Found: Si, 14.54, 14.53; mol. wt., 752, 760.

A second reaction was made with 10.0 gm. (0.012 mole)
of XIII in 300 ml. of propyl alcohol. The yield of the
octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane,
m.p. 222-224°C, was 43.5% (4.0 gm.). Also obtained was
4.5 gm. (42.5%) of solid melting over the range 58-70°C.
Recrystallization from propyl alcohol gave 1.9 gm. of
1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxy-
trisiloxane, m.p. 79-80°C, identified by a mixture m.p.
and infrared spectrum comparison with the previously
prepared sample.

Hydrolysis of 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexa-
phenyl-5-propoxytrisiloxane (XVI). Refluxing 10.0 gm.
(0.013 mole) of XVI in 100 ml. of propyl alcohol for
15 hours resulted in a 95% (9.5 gm.) recovery of the
starting material, m.p. 78-80°C. No other isolable
crystalline products were found.

A second treatment was made with 8.7 gm. (0.01 mole)
of XVI in 150 ml. of propyl alcohol which was saturated
with anhydrous hydrogen chloride. After refluxing 24
hours, the reaction mixture was cooled to 5°C for 2 hours
and then filtered to give 0.35 gm. (4%) of solid melting
over the range 74-125°C. Concentration of the filtrate
gave any additional 7.1 gm. (78.5%) of solid melting
over the range 76-118°C. The solids were extracted
several hours with 20 ml. of cold petroleum ether (b.p.
60-70°C) leaving 0.65 gm. (8.5%) of octaphenyl-1,3,5-
trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 222-223°C.
Evaporation of the filtrate and recrystallization of the
residue in propyl alcohol yielded 5.9 gm. (68%) of
starting material, m.p. 79-81°C.

In a third reaction, anhydrous hydrogen chloride
was bubbled at a slow constant rate through 100 ml. of
refluxing propyl alcohol containing 4.7 gm. (0.0054 mole) of
XVI for 6 to 7 hours. The reaction was then cooled and
the mixture filtered to give 2.3 gm. (55.5%) of octa-
phenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p.
223-224°C. Concentration of the filtrate gave 0.4 gm.
(9.5%) of crude material, m.p. 176-180°C. No attempt
was made to purify this fraction.

The pyrolysis of 1-(diphenylpropoxysilyl)-1,1,3,3,5,5-hexaphenyl-5-propoxytrisiloxane. (XVI). A 1.76 gm. (0.001 mole) sample of XVI, placed in a long open tube, was put in a furnace in such a way that the top of the tube protruding from the furnace remained cool. The tube was then heated at 160°C for 2 hours, at 200°C for 12 hours and at 300°C for 9 hours. During the last 7 hours the liquid in the tube turned to a light straw color and several drops of a liquid condensed on the upper portion of the tube. The weight loss of the pyrolized material was 0.06 gm. Upon cooling the reaction mixture a viscous liquid remained which was soluble in petroleum ether (b.p. 60-70°C) and propyl alcohol. IXa is insoluble in the former solvent and the latter precipitates XVI. Organic solvents were removed from the resin with a heating pistol at 58°C and 1 mm. pressure. An infrared spectrum of the residue was similar to that of the starting material.

Hydrolysis of 1,6-dichloro-1,1,3,3,4,4,6,6-octaphenyl-2,5-dioxa-1,3,4,6-tetrasilahexane (XIV). A 4.2 gm. (0.005 mole) sample of XIV was heated in propyl alcohol, 150 ml., at 97°C for 4 to 5 hours. Cooling and filtering off the solid provided 0.2 gm. of solid, m.p. 217-219°C. Concentration of the filtrate gave the following fractions: 1.2 gm., melting over the range 104-144°C, 2.0 gm., melting over the range 97-137°C, and 0.1 gm., 218-219°C. Recrystallization in petroleum ether (b.p. 60-70°C) yielded 0.4 gm. (10%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 223-224°C, identified by infrared spectra comparison and mixture m.p. A second pure fraction weighed 1.4 gm. (34%), m.p. 106-107°C, and was identified as 5,5,7,7,8,8,10,10-octaphenyl-4,6,9,11-tetraoxa-5,7,8,10-tetrasilatetradecane (XVII). The compound showed a $\lambda_{max.}$, 243 mμ in cyclohexane in the ultraviolet region. An infrared spectrum (in CS_2) gave absorptions in μ at: 3.27, 3.37, 3.47 (m), 5.12, 5.30, 5.48, 7.20, 7.28, 7.68, 7.93 (w), 8.42 (m), 8.75, 8.92, 9.04 (s triplet), 9.53, 9.75 (s), 9.85 (sh), 10.03, 12.07 (m), 13.58, 13.96, 14.35 (s), 14.67 (m).

Anal. Calcd. for $C_{54}H_{54}O_4Si_4$: Si, 12.77; mol. wt., 879. Found: Si, 12.87, 12.82; mol. wt., 833, 875, 882, 909.

b. With hydrogen chloride. Hydrogen chloride gas was added to 150 ml. of propyl alcohol at a slow steady rate for 10 min. The temperature was then 45°C. XIV, 7.0 gm. (0.008 mole), was added and the mixture refluxed for 7 hours with slow addition of the hydrogen chloride. Upon cooling and standing two days, 4.9 gm. (79%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane, m.p. 223-224°C was obtained by filtration. No other crystalline materials were isolated.

Preparation of 1,7-dichloro-1,1,3,3,5,5,7,7-octaphenyl-tetrasiloxane.

a. In carbon tetrachloride-petroleum ether. Chlorine was added at 190 ml./min. for 20 min. (3.8 1; 0.015 mole) to a mixture containing 1.9 gm. (0.0024 mole) of IXa in 60 ml. of carbon tetrachloride and 50 ml. of petroleum ether (b.p. 60-70°C). Product isolation as previously described gave 1.75 gm. (84%) of crude product, melting over the range 96-104°C. Partial hydrolysis occurred during recrystallization to give impure fractions melting above 200°C. Only a small amount, 0.5 gm. (25%), m.p. 96-97°C, of 1,7-dichloro-1,1,3,3,5,5,7,7-octaphenyltetrasiloxane was obtained. The ultraviolet spectrum of the dichloride in cyclohexane showed λ_{max}, 271 mμ, 264, 259, 254. The infrared spectrum (in CS_2) contained absorptions in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.30, 7.53, 7.70, 7.94 (w), 8.44 (m), 8.90 (s), 9.22 (m), 9.50 (s), 9.75, 10.03 (m), 13.57, 13.95, 14.41 (s).

Anal. Calcd. for $C_{48}H_{40}Cl_2O_3Si_4$: Si, 13.23; mol. wt., 848. Found: Si, 13.36, 13.41; mol. wt., 827, 816, 824.

b. In petroleum ether. Chlorine was added at 200 ml./min. for 21 min. (4.2 1; 0.017 mole) to a suspension of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa), 3.9 gm. (0.005 mole) in 100 ml. of petroleum ether (b.p. 60-70°C). After treatment with chlorine for 9 min. the temperature rose rapidly to 45°C and an ice-bath was used to hold the temperature at 26-29°C. The excess of chlorine was removed under reduced pressure and the mixture filtered to obtain 1.2 gm. (28%) of crude product, m.p. 98-101°C. Concentration of the filtrate afforded three additional fractions: 1.2 gm. (28%), m.p. 98-100°C, 0.9 gm. (22%), m.p. 96-98°C, and 0.4 gm. of solid of which the major portion melted at 97-100°C with the balance at 170°C. The total crude yield was 3.7 gm. (87%) with a 3.3 gm. (78%) yield of pure 1,7-dichloro-1,1,3,3,5,5,7,7-octaphenyltetrasiloxane, m.p. 98-100°C.

Preparation of octaphenylcyclotetrasiloxane.   Hydrogen
chloride was added for 45 min. at a slow constant rate
to 140 ml. of propyl alcohol.   At 50°C a total of 3.9 gm.
(0.0046 mole) of 1,7-dichloro-1,1,3,3,5,5,7,7-octaphenyl-
tetrasiloxane (XVIII) was added: 2.2 gm. (0.026 mole)
of XVIII from the chlorination of the cyclic trioxide
IXa obtained by hydrolysis of 1-(chlorodiphenylsilyl)-3-
(chlorodiphenylsiloxy)-1,1,3,3-tetraphenyldisiloxane (XIII)
and 1.7 gm. (0.02 mole) of XVIII from the chlorination of
the cyclic trioxide IXa obtained by hydrolysis of 1,6-
dichloro-1,1,3,3,4,4,6,6-octaphenyl-2,5-dioxa-1,3,4,6-
tetrasilahexane (XIV).   The mixture was then heated at
90°C for 6 hours, cooled, allowed to stand several days
and the solid filtered off to obtain 3.0 gm. (82%) of
crude octaphenylcyclotetrasiloxane, m.p. 196-200°C.
Concentration of the filtrate provided only a trace of
additional solid material.   Recrystallization of 2.0 gm.
in petroleum ether (b.p. 80-115°C) gave 1.8 gm. of pure
octaphenylcyclotetrasiloxane identified by mixture m.p.
(200-202°C) with a sample prepared by M. V. George.[124]

In a separate experiment 0.5 gm. of XVIII was re-
fluxed in 15 ml. of propyl alcohol for 2-3 hours.   Cooling
precipitated 0.1 gm. of solid, m.p. 203-210°C.   Concen-
tration of the solution gave, after several days, a few
large clear crystals (approximately 0.1 gm.) melting at
59-60°C.   The ultraviolet spectrum in cyclohexane showed
λmax., 270 mμ, 264, 258, 252. 246.   The infrared spec-
trum indicated that the compound is probably 1,1,3,3,5,5-
7,7-octaphenyl-1,7-dipropoxytetrasiloxane and (in CS_2)
showed absorptions in μ at: 3.28, 3.38, 3.50 (m), 5.13,
5.31, 5.50, 7.22, 7.31, 7.54, 7.71, 7.95 (w), 8.46 (m),
8.92, 9.22, 9.54 (s), 9.75, 10.03, 12.03 (m), 13.57, 13.98,
14.37 (s), 14.65 (m).

Reaction of octaphenylcyclotetrasilane and nitrobenzene.
A 3.65 gm. (0.005 mole) sample of octaphenylcyclotetra-
silane was added to 50 ml. of nitrobenzene and the mix-
ture heated at reflux for 30 min.   Cooling and addition
of 75 ml. of ethyl alcohol gave no crystalline products.
The solvents were then removed by distillation under reduced
pressure.   The residue was dissolved in acetone and 50 ml. of
ethyl alcohol was added.   Upon standing, 2.5 gm. (68%) of
dark brown crystals precipitated, m.p. 185-208°C.   Re-
crystallization from acetone yielded 0.45 gm. (12%) of
a compound having a constant m.p. of 245-246°C.   This

sample was used for an X-ray powder photograph which was found to be identical to the powder photograph of VIII, m.p. 256-257°C, obtained from the hydrolysis of XIII (see above). An ultraviolet spectrum of the above sample gave a $\lambda_{max.}$ (in cyclohexane) 245 mμ (sh). The infrared spectrum gave absorptions (in CS_2) in μ at: 3.27 (m), 5.13, 5.30, 5.50, 7.3, 7.55, 7.72, 7.95 (w), 8.46 (m), 8.91, 9.0, 9.07 (s triplet), 9.43 (sh), 9.65, 9.71, 10.06 (m), 13.63, 14.00, 14.40 (s), 14.80 (m).

A second mixture of octaphenylcyclotetrasilane, 21.9 gm. (0.3 mole) and 100 ml. of nitrobenzene was heated to 165°C. The reaction then became vigorously exothermic and the temperature rose to 208°C in less than one minute with a rapid reflux observed for several min. After heating at reflux for an additional 15 min. the mixture was then cooled. Removal of the solvent by distillation under reduced pressure and addition of 50 ml. of acetone to the residue provided upon standing 4.9 gm. (22.4% based on starting material) of solid, m.p. 234-237°C. The addition of 30 ml. of ethyl alcohol gave an additional 6.2 gm. (28.3%) of a black crystalline solid. Repeated recrystallizations from acetone and from petroleum ether (b.p. 80-115°C) gave many fractions. Several grams were obtained which melted at 245-246°C. After several re-crystallizations this m.p. rose to 248-250°C. The melting point of the major fraction was 245-247°C after seven recrystallizations. Small fractions having lower and higher melting points were obtained after each recrystallization. The infrared spectrum of the major fraction (in CS_2) gave absorptions in μ at 9.43 (sh), 9.65, 9.81 and 10.06 in the Si-O-Si band region. The absorptions at 9.65 and 10.06 μ are believed to be due to the Si-Ph absorption. The band at 9.65 μ appears at 9.75 μ for larger ring siloxanes and is shifted to 9.65 μ for six-membered ring compounds showing an Si-O-Si absorption at 9.8-9.9 μ. Lower melting pure fractions, 1.3 gm., m.p. 230-232°C, and 0.15 gm., m.p. 219-220°C, were obtained. A mixture m.p. with the higher melting fraction and IXa was not depressed. The infrared spectra of these two lower melting fractions (in CS_2) showed an Si-O-Si bond absorption at 9.43 μ identical to IXa.

A third reaction mixture of Ia, 21.9 gm. (0.03 mole), in 100 ml. of nitrobenzene was slowly heated to 140°C in 1.5 hours. The reaction was then cooled and 19.1 gm. (87%) of the starting material, m.p. 320-327°C, was recovered by filtration. Distillation of the filtrate

under reduced pressure and addition of 15 ml. of acetone provided 0.7 gm. (3.2%) of solid melting over the range 262-280°C (block preheated to 250°C). Ethyl alcohol, 20 ml., was then added and an additional 1.1 gm. (5%) of crystalline solid was obtained. The overall yield of solids based on starting material was 95%. Recrystallization of the last two fractions from acetone gave 0.7 gm. (3%) melting at 255-257°C (block preheated to 250°C), 0.25 gm. (1%) melting at 244-246°C and three other fractions totaling 0.6 gm. (2.5%), m.p. 252-255°C. A mixture m.p. with the first fraction and VIII, m.p. 256-257°C was not depressed. The infrared spectrum (in CS_2) showed an Si-O-Si bond absorption at 9.80μ characteristic of a six-membered ring (see Table I). An infrared spectrum of the second fraction, m.p. 244-246°C showed Si-O-Si bond absorptions at 9.43 (sh) and 9.80μ similar to mixtures of IXa and VIII (see Table I).

Octaphenyloxacyclopentasilane (IV) and nitrobenzene. A mixture of 7.5 gm. (0.01 mole) of IV and 50 ml. of nitrobenzene was heated to the boiling point over a period of 40 min. After refluxing for 10 min. the mixture was allowed to cool and the solvents were removed by distillation under reduced pressure. Treatment of the black tarry residue with acetone and acetone-ethanol mixtures gave three fractions of solid: 1.5 gm., m.p. 270-274°C; 3.6 gm., m.p. 224-228°C and 0.7 gm. melting over the range 208-222°C. The overall yield of solid obtained, based on starting material, was 5.8 gm. (78%). Recrystallization from acetone gave 0.5 gm. of pure octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane (VIII) identified by a mixture m.p. 256-257°C and infrared spectrum comparison with an authentic sample. Several other fractions gave constant sharp melting points at the same and at lower temperatures but infrared spectra comparisons indicated they were mixtures of five-, six-, and seven-membered ring compounds (see Table I).

A duplicate reaction was heated at reflux temperature for 2 hours prior to the usual work-up, and gave 3.4 gm. (45% based on starting material) of crystalline solids. Recrystallizations gave 2.7 gm. (34.5%) of octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane (IXa), m.p. 221-222°C. The ultraviolet spectrum showed a λ_{max} 239 mμ in cyclohexane. The infrared spectrum (in CS_2) gave the following absorptions in μ : 3.27 (m), 5.12,

5.30, 5.50, 7.30, 7.54, 7.68, 7.94, 8.43 (w), 8.91, 8.97
(s doublet), 9.06 (w sh), 9.44, 9.76 (s), 10.02 (m),
13.58, 13.96, 14.37 (s), 15.45 (m).

Anal. Calcd. for $C_{48}H_{40}O_3Si_4$: Si, 14.44; mol. wt.,
777. Found: Si, 14.51, 14.56; Mol. wt., 791.

Since this compound previously prepared by the
hydrolysis of XIII gave a m.p. of 231-232°C X-ray powder
photographs were taken of the two compounds. The X-ray
powder photographs were not identical. Fractions of
XIa, m.p. 221-222°C, were later obtained from the hydrolysis
of XIV, and the mixture m.p. of this sample and the above
product was not depressed. No chemical, analytical or
spectral evidence was found to indicate the compound was
not IXa.

Octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane and
nitrobenzene. A 3.8 gm. sample of octaphenyl-1,3-dioxa-
2,4,5,6-tetrasilacyclohexane (VIII) (0.005 mole) was
heated at reflux for 2 hours in 50 ml. of nitrobenzene.
The mixture was then cooled and filtered to obtain 3.1 gm.
(82%) of solid material, m.p. 242-244°C. Concentration
of the filtrate provided 0.35 gm. (9%) of solid material
melting over the range 220-240°C. Recrystallization yielded
2.9 gm. (76%) of pure VIII, m.p. 253-255°C, and a trace of
solid melting at 214-226°C.

A second treatment of VIII, 3.8 gm. (0.005 mole),
with 50 ml. of refluxing nitrobenzene for 24 hours gave no
insoluble material upon cooling and standing for several
hours. Distillation of the solvent under reduced pressure
and addition of acetone to the black residue also gave no
precipitate upon standing. Evaporation of the acetone
and addition of 40 ml. of ethyl alcohol provided two crops
of crystalline dark brown solids, 1.6 gm. (42% based on
starting material) m.p. 174-180°C, and 0.3 gm. (8%) melt-
ing over the range 162-172°C. The solids were dissolved
in acetone and decolorized with activated charcoal. The
acetone was then evaporated and the residue recrystallized
from petroleum ether (b.p. 80-115°C). A 0.2 gm. sample
of a white crystalline solid was obtained, m.p. 189-193°C.
A mixture m.p. with an authentic sample of hexaphenylcyclo-
trisiloxane, m.p. 192-193°C, prepared by G. Kolb[125] melted
at 191-193°C. The ultraviolet spectrum of this and all
fractions obtained showed $\lambda_{max.}$ in cyclohexane at 254 mμ,
259, 264.5, 270 indicating that no polysilane compounds

were present. From a 0.45 gm. fraction, m.p. 193-195°C, pure crystals of octaphenylcyclotetrasiloxane were hand-picked with tweezers and the mixture m.p. with an authentic sample,[124] m.p. 204-205°C, was not depressed. An infrared spectrum was also used to identify these two products. Since these two compounds are known to form eutectic mixtures and exhibit polymorphism[111],[113] no further attempts to separate the products were made.

Octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane and nitrobenzene. A mixture containing 75 ml. of nitrobenzene and 6.85 gm. (0.009 mole) of octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (VIIa) was heated at 205°C for 4 hours. The reaction mixture was then cooled and upon standing overnight 6.55 gm. (96%) of the starting material was recovered, m.p. and mixture m.p. 227-229°C. Concentration of the filtrate gave 0.1 gm. (1.5%) of black crystalline solid, m.p. 216-220°C.

In a second reaction 5.35 gm. (0.007 mole) of VIIa was heated at reflux for 24 hours in 50 ml. of nitrobenzene. Upon cooling and standing no precipitate was formed. Distillation of the solvent under reduced pressure and addition of 50 ml. of acetone also provided no precipitate upon standing. Most of the acetone was allowed to evaporate and 40-50 ml. of ethyl alcohol was added. A 2.15 gm. (40% based on starting material) sample of brown crystals was obtained melting over the range 165-178°C. Evaporation of the filtrate to 10 ml. and addition of 50 ml. of ethyl alcohol yielded no more crystalline solids upon standing several weeks. The residue obtained by removal of the solvent from the filtrate consisted of a black tar. This was soluble in acetone but formed an insoluble oil in petroleum ether (b.p. 60-70°C). Recrystallization of the solids from acetone and petroleum ether (b.p. 80-115°C) gave 0.4 gm. of pure octaphenylcyclotetrasiloxane, m.p. 204-205°C. It was identified by mixture m.p., comparison of the infrared spectra, and by an ultraviolet spectrum in cyclohexane, $\lambda_{max.}$, 253 mμ, 259, 269.5, 270.5. Also obtained was 0.6 gm. of hexaphenylcyclotrisiloxane, which was identified by a mixture m.p., infrared spectrum and by the ultraviolet spectrum in cyclohexane, $\lambda_{max.}$, 253.5 mμ, 259.5, 264.5, 270. Other fractions obtained; 0.65 gm. melting over the range 160-175°C and 0.6 gm. melting over the range 179-188°C, appeared to be eutectic mixtures of these two compounds as indicated by comparison of the infrared spectra.

Decaphenylcyclopentasilane and nitrobenzene. A 10 gm. (0.011 mole) sample of decaphenylcyclopentasilane (IIa) and 75 ml. of nitrobenzene were refluxed for 24 hours. Removal of the solvents by distillation under reduced pressure and addition of 50 ml. of acetone to the residue gave 2.1 gm. (21%) of IIa, m.p. 468-474°C. The tarry black filtrate was partly decolorized with activated charcoal and approximately 0.1 gm. of crystalline solids were removed with a spatula from the sides of the flask as the acetone evaporated. Recrystallization of these crystals gave impure solids having melting ranges of 178-180°C, 160-164°C and 166-184°C. Ultraviolet spectra of the solids gave λ max. 253.5 mμ, 259, 264, 270.5 showing that the solid contained no polysilanes. An infrared spectrum showed Si-phenyl absorptions at 8.88, 8.92, and 9.68 and Si-O-Si bond absorptions at 9.25 (w) and 9.88 μ. These absorptions were identical to those in the spectrum of a mixture of octaphenylcyclotetrasiloxane and hexaphenylcyclotrisiloxane. No other crystalline solids were obtained upon treatment of the tarry residues with ethanol or petroleum ether (b.p. 60-70°C).

Dodecaphenylcyclohexasilane and nitrobenzene. (Attempted). Dodecaphenylcyclohexasilane, 2.0 gm. (0.0018 mole) was heated in 50 ml. of refluxing nitrobenzene for 24 hours. The mixture was then cooled and filtered to give a quantitative recovery (2.0 gm.) of starting material, m.p. 492-500°C.

Hexaphenyldisilane and nitrobenzene. (Attempted). A 10.4 gm. sample of hexaphenyldisilane (0.02 mole) was heated at 180-200°C for 24 hours in 75 ml. of nitrobenzene. The reaction mixture was then cooled and filtered to give 9.95 gm. (96%) of starting material, m.p. and mixture m.p. 368-370°C. The filtrate was concentrated to give an additional 0.1 gm. (1%) melting over the range 340-380°C.

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Iowa State University Ames, Iowa	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

ORGANO-METALLIC AND ORGANO-METALLOIDAL HIGH-TEMPERATURE LUBRICANTS AND RELATED MATERIALS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Summary Report (15 December 1964 to 15 December 1965)

5. AUTHOR(S) *(Last name, first name, initial)*

Gilman, Henry

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
December 15, 1965	79	125

8a. CONTRACT OR GRANT NO. AF 33(615)-2368	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 7342	AFML-TR-64-383, Pt. II
c. Task No. 734201	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Nonmetallic Materials Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, WPAFB, O.

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This report describes some entirely novel types of organo-silicon compounds. They are primarily polyfunctional monomers. The functional groups may be alike or unlike, and the symmetry with some is unique in being of the highest possible order. These polyfunctional organosilicon monomers should provide avenues to the preparation of polymers with diverse and promising properties. Among the polyfunctional types are such highly reactive species as $(HMe_2Si)_4Si$ and $(HMe_2Si)_3SiLi$.

DD FORM 1473
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